Development of High Temperature Liquid Chromatography for Chemical Composition Separation of Polyolefins

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Publications

1. "Characterization of ethylene-methyl methacrylate and ethylene-butylacrylate copolymers with interactive liquid chromatography"
   R. Chitta, R. Brüll, V. Monteil, C. Boisson, E. Grau, A. Leblanc, T. Macko
   Macromolecular Symposia 298 (2010) 191-199

2. "Elution behaviour of polyethylene and polypropylene standards on carbon sorbents"
   R. Chitta, T. Macko, R. Brüll, G. Kalies
   Journal of Chromatography A 1217 (2010) 7717-7722

3. "Separation of ethylene-propylene copolymers and ethylene-propylene-diene terpolymers using high temperature interactive liquid chromatography"
   R. Chitta, T. Macko, R. Brüll, G. Van Doremaele, L. C. Heinz
   Journal of Polymer Sciene Part A: Polymer Chemistry 49 (2011) 1840-1846

4. "Separating ethylene-propylene-diene terpolymers according to the content of diene by HT-HPLC and HT 2D-LC"
   R. Chitta, A. Ginzburg, G. van Doremaele, T. Macko, R. Brüll
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5. "Interactive liquid chromatography of olefin based elastomers"
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6. "Carbonaceous sorbents for high temperature liquid interactive chromatography of polyolefins"
   R. Chitta, R. Brüll, T. Macko, M. Miller, R. Cong, W. deGroot
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Posters

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   Siegen, Germany, April 2010

2. "Separation of polyethylene and polypropylene with high-temperature liquid chromatography"
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3. "Separation of polyethylene and polypropylene by adsorption liquid chromatography"
   3rd Blue Sky conference on Catalytic Olefin Polymerization
   Sorrento, Italy, June 2010

4. "Adsorption liquid chromatography of polyethylene"
   16th International Symposium on Separation Science
   Rome, September 2010

5. "New sorbent/solvent systems for separation of polyethylene and polypropylene with interactive liquid chromatography"
   3rd International Conference on Polyolefin Characterization
   Shanghai, November 2010

6. “The first interactive liquid chromatography of EPDM polymers”
   3rd International Conference on Polyolefin Characterization
   Shanghai, November 2010

7. “Application of high temperature adsorption liquid chromatography for chemical composition separation of polyolefins”
   5th International Symposium on Separation and Characterization of Macromolecules Amsterdam, January 2011

8. “HPLC of hydrogenated polybutadienes and hydrogenated styrene-butadiene block copolymers”
   5th International Symposium on Separation and Characterization of Macromolecules Amsterdam, January 2011

9. “Chromatographic characterization of amorphous and semicrystalline polyolefin elastomers”
   4th Asian Polyolefin Workshop
   Bangkok, July 2011

10. “Interactive liquid chromatography: A new tool to characterize EP and EPDM rubbers”
    Advances in Polyolefins
    California, September 2011

11. “High temperature liquid chromatography and HT 2D-LC of polyolefins”
    3rd International multicomponent polymer conference
    Kerala, India, March 2012

12. “Separation of LLDPE samples with adsorption liquid chromatography”
    8th International colloquium on heterogeneous Ziegler-Natta catalysts
    Kanazawa, Japan March 2012

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1 Summary in German

Polyolefine sind gemessen am Volumen die bedeutendsten synthetischen Polymere. Ihre globale Produktion hat in den letzten Jahren kontinuierlich zugenommen und es ist zu erwarten, dass sich dies in Zukunft weiter fortsetzen wird. Treibende Kraft dabei sind neue Verarbeitungstechnologien und Syntheseverfahren, welche entwickelt werden, um den Anforderungen des Marktes nachzukommen.

Polyolefine können wie jedes andere synthetische Polymer verschiedene Arten molekularer Heterogenitäten zeigen. Diese zu messen ist der Schlüssel um Struktur↔Eigenschafts Beziehungen zu entwickeln und mit deren Hilfe die Anwendungseigenschaften der Endprodukte maßzuschneidern. Die Molmassenverteilung (*Molar Mass Distribution*, MMD) und die Verteilung der chemischen Zusammensetzung (*Chemical Composition Distribution*, CCD) sind die beiden grundlegenden molekularen Größen, die im Fall von Polyolefinen von entscheidendem Interesse sind, da sie den größten Einfluss auf die Eigenschaften des Endprodukts haben.

Flüssigchromatographie ist bei Copolymeren und Polymeren, die bei Raumtemperatur löslich sind, ein wichtiges Werkzeug um Heterogenitäten hinsichtlich Molmasse und chemischer Zusammensetzung zu bestimmen. Während die Größenausschlusschromatographie (*Size Exclusion Chromatography*, SEC) routinemäßig zur Bestimmung der MMD genutzt wird, findet die Hochleistungsflüssigschromatographie (*High Performance Liquid Chromatography*, HPLC) weithin Anwendung zur Bestimmung der CCD.

Die HPLC kann potentiell einen schnellen Ansatz zur Charakterisierung der CCD von Polyolefinen liefern, ohne einige der Nachteile der etablierten Techniken, wie *Temperature Rising Elution Fractionation* (TREF) oder Kristallisationsfraktionierung (*Crystallization Analysis Fractionation*, CRYSTAF), die auf Kristallisation basieren. Jedoch sind aufgrund ihrer teilkristallinen Natur bei vielen Polyolefinen Temperaturen > 100 °C nötig, um diese zu lösen. Zusätzlich zu der beschränkten Zahl an Lösungsmitteln, welche für Polyolefine in Frage kommen, existiert nur ein unzureichendes Verständnis der Wechselwirkungen gelöster Polyolefine mit den Sorbentien und Solventien. Diese Beschränkungen machen es extrem

herausfordernd neue Sorbent/Solvent-Systeme für die HPLC von Polyolefinen zu identifizieren.

Mit dem Ziel neue Sorbent/Solvent-Systeme für die Hochtemperatur (HT)-HPLC von Polyolefinen zu identifizieren, wurden im Rahmen dieser Arbeit neue mobile und stationäre Phasen getestet. Ausgehend von der Fähigkeit von Hypercarb, Polyolefine hinsichtlich ihrer Zusammensetzung und Mikrostruktur zu fraktionieren, war es Ziel, alternative Kohlenstoff-basierte Sorbentien auf ihre Eignung als stationäre Phase zur Hochtemperatur (HT)-HPLC von Polyolefinen zu bewerten. Als mobile Phase wurden polare Lösungsmittel (Aromaten und Alkohole) getestet. Die Adsorbtionseigenschaften von Kohlenstoff-basierten Sorbentien für Polyolefine wurden in systematischer Weise verglichen und quantitative Informationen über die Adsorption von Polyethylen (PE)- und Polypropylen (PP)- Standards gesammelt, um den Einfluss von Lösungsmittel, Molmasse und Mikrostruktur des Polymers auf dessen Adsorption besser zu verstehen.

Besondere Aufmerksamkeit wurde auf den Einfluss der Molmasse auf die Elution von Polymeren und die Fähigkeit des chromatographischen Systems, Stereoisomere im Fall von PP zu unterscheiden, gelegt, da dies die herausragenden Eigenschaften Kohlenstoff-basierter Sorbentien sind. Es wurde gezeigt, dass PE und/oder PP in unterschiedlichem Ausmaß adsorbieren, abhängig vom betrachteten Sorbent/Solvent-Paar. Die Art des Kohlenstoff-Sorbents beeinflusst das Ausmaß der Adsorption stark, wobei Hypercarb eine größere Adsorptionsneigung zeigt als andere Kohlenstoff-basierte Sorbentien wie beispielsweise Aktivkohle oder exfoliierter Graphit. Das chromatographischen System Hypercarb/Alkohol (C7-C9)→1,2,4-Trichlorbenzol (TCB) ermöglicht es bei 160 °C, alle Stereoisomeren von PP selektiv zu adsorbieren und desorbieren. Die Retention der Stereoisomere nahm mit der Polarität des Alkohols zu.

Die entwickelten neuen chromatographischen Systeme wurden eingesetzt, um Copolymere aus Ethylen und 1-Olefinen hinsichtlich ihrer chemischen Zusammensetzung zu trennen. Die Untersuchungen zeigten dass Kurzkettenverzweigungen (*Short Chain Branches*, SCB) eine wichtige Rolle bei der Adsorption von Polyolefinen auf Kohlenstoff-basierten stationären Phasen spielen,

indem sie die Retention der Makromoleküle vermindern. Interessanterweise ist im Fall von 1-Octadecen als Comonomer die Verminderung der Adsorption geringer als bei Comonomeren, welche Kohlenstoffeinheiten von C8 oder weniger enthielten. Dies deutet darauf hin, dass die SCB selbst auch zur Adsorption der Makromoleküle beitragen, wenn diese genügend lang sind.

Erstmals wurden amorphe Ethylen-Propylen- (EP) Copolymere und Ethylen-Propylen-Dien-Terpolymere (EPDM) mittels HT-HPLC nach ihrer chemischen Zusammensetzung getrennt. Hypercarb in Kombination mit einem Lösungsmittelgradienten 1-Decanol→TCB wechselwirkte spezifisch mit den Ethyleneinheiten. Daher eluieren die EP-Copolymere im Gradienten entsprechend ihres Ethylengehalts. Im Fall von EPDM war das Retentionsvolumen eine Funktion des Gehalts sowohl an Ethylen als auch Ethyliden-2-Norbornen (ENB). Der alleinige Beitrag von ENB zur chromatographischen Retention wurde durch Berechnung der Differenz der Elutionsvolumina zwischen dem EPDM und einem EP-Copolymer, welches einen äquivalenten Gehalt an Ethylen aufwies, quantifiziert. Die Untersuchung der Trennung von EPDM mit anderen Dienen deutete darauf hin, dass der Beitrag des Diens zur Retention auch von dessen Art abhängt. Erstmals konnte durch Kopplung der HT-HPLC und SEC die Verknüpfung zwischen CCD und MMD in EPDM aufgeklärt werden.

HT-HPLC ist eine neue Methode für die Trennung von PE, PP und anderen Polyolefinen nach ihrer chemischen Zusammensetzung. Die vorgestellte Arbeit erweitert die Zahl der für die Trennung von Polyolefinen geeigneten Sorbent/Solvent-Systeme signifikant. Einige davon besitzen das Potential zur Anwendung Anwendung in der Routineanalytik und/oder präparativen LC-Trennung von Polyolefinen. Beispielsweise ermöglicht es das System Hypercarb/2-Octanol→TCB, Ethylen-Propylen-Copolymere nach ihrer chemischen Zusammensetzung in einem Bereich von 0 - 100 Gew.- % Ethylen zu trennen. Im Unterschied TREF und CRYSTAF benötigt die HT-HPLC eine geringere Menge Proben, Lösungsmittel und eine kurze Analysenzeit. Darüber hinaus können sowohl amorphe als auch teilkristalline Polyolefine getrennt werden, da die HT-HPLC auf selektiver Adsorption und Desorption beruht.

2 Introduction

2.1 Significance of Polyolefins

Polyolefins are the most widely used class of commodity thermoplastics and constitute by volume more than 50 % of all synthetic polymers produced annually. The worldwide production of polyolefins has grown at a substantial rate over the past few years [1], and is expected to continue to do so in future as new technologies and synthesis procedures are constantly developed to satisfy commercial demands. Their excellent properties like high mechanical strength, chemical stability, flexibility, processability, along with their non-toxicity, low cost and easily available raw materials have led to this success story. The most important polyolefins are the homopolymers polyethylene (PE) and polypropylene (PP), followed in commercial significance by copolymers of ethylene with olefinic comonomers. Copolymers of ethylene and propylene (EP) and ethylene propylene diene terpolymers (EPDM) are commercially important elastomers. In the following the synthesis, structure and major applications of the individual classes will be described. Figure 2.1 illustrates the global demand and production of PE and PP for 2006 with forecasts for the year 2020 [2].

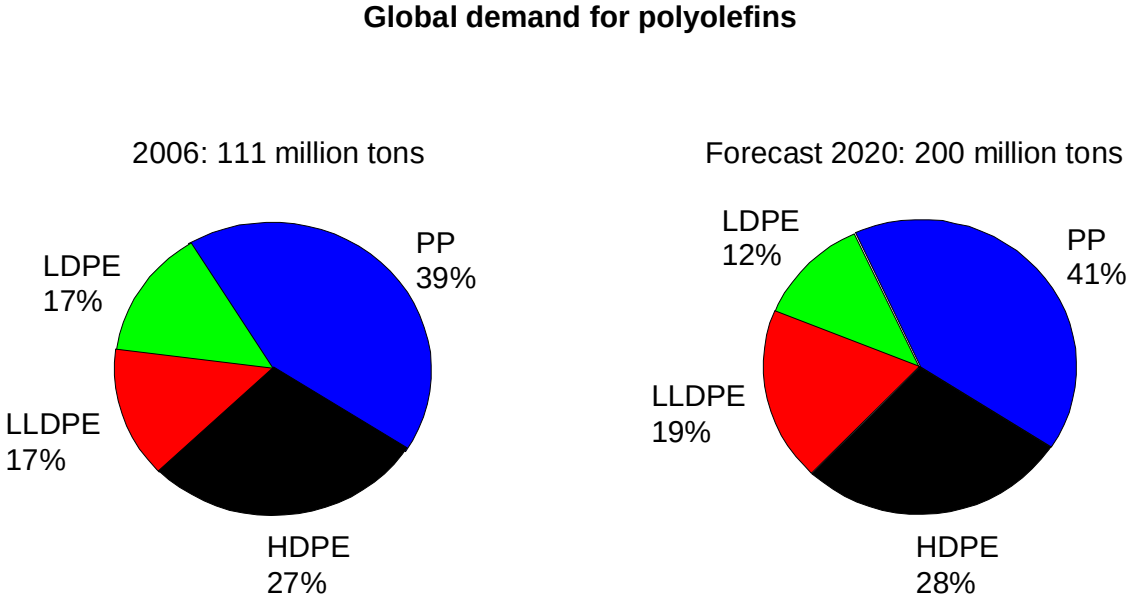


Figure 2.1: Global demand for PE and PP.

2.1.1 Polyethylene

PE is by volume the world's largest commodity synthetic polymer. Of primary commercial significance are the homopolymer and copolymers of ethylene with up to 20 % of 1-olefinic comonomer like 1-butene, 1-hexene, and 1-octene. The latter is used to impart to the final product some desired property which would not be achievable by the homopolymer. Traditionally, based on their density and manufacturing process, PE is classified into three major groups (Figure 2.2): High Density (HDPE), Low Density (LDPE), and Linear Low Density (LLDPE). The density range of these PE grades is shown in Table 2.1.

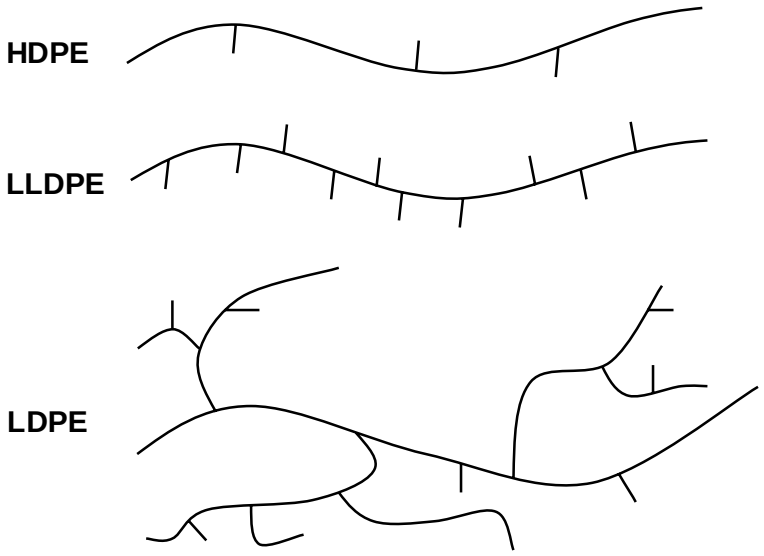


Figure 2.2: Schematic representation of the different types of PE. In the sequence from top to bottom: HDPE (low content of short chain branches, i.e. *n*-alkyl groups with less than 6 carbons); LLDPE (many short chain branches); LDPE (many short and long chain branches).

Table 2.1: Density range of various types of polyethylene.

Type of PE	Density range (g/cm^3)
HDPE	0.945-0.965
LDPE	0.890-0.940
LLDPE	0.910-0.925
VLDPE, ULDPE*	0.87-0.915

*VLDPE and ULDPE are a family within LLDPE having a high comonomer content and relatively low density than LLDPE that bridges the density gap between LLDPE of 0.915 g/cm^3 to ethylene/propylene rubber of 0.85 g/cm^3 [3].

PE was originally commercialized by Imperial Chemical Industries (London, England) in the 1930s with the use of a high-pressure free-radical polymerization process [4]. This process produced a highly branched material containing both short chain branches (SCB) generated by chain backbiting and long chain branches (LCB) generated by chain transfer to polymer, due to the radical chain transfer processes. The range of properties and accordingly the applications were limited. This class of PE is called low-density polyethylene (LDPE) [5]. It is widely used for blow molding applications to produce heavy-duty sacks, refuse bags, carrier bags and general packaging [6].

The discovery of Ziegler-Natta catalysts triggered a new era in polyolefin research which lead to a rapid expansion of their industrial production and broadened the application range substantially. These catalysts were first discovered in the laboratories of K. Ziegler in 1953 to produce HDPE [7], which then became commercially available since the mid 1950's. HDPE is a linear ethylene homopolymer with no or very low levels of SCB [5]. Compared to LDPE and LLDPE, HDPE is far more crystalline and consequently has higher density. In addition to that it also has increased tensile strength, stiffness, chemical resistance, and upper temperature range. However, HDPE has reduced low temperature impact strength, elongation and resistance towards stress cracking [8].

Copolymerizing ethylene with a small amount of 1-olefin, such as 1-butene, 1-hexene, 4-methyl-1-pentene, or 1-octene yields copolymers with a lower density compared to HDPE. Their density may vary in a wide range depending on the nature and content of comonomer. Due to their essentially linear architecture, these copolymers are referred to as Linear Low Density Polyethylene (LLDPE). LLDPE (as well as ULDPE and VLDPE) and HDPE are produced at low pressure (20 - 30 bar) and low temperature (80 - 120 °C) via transition metal catalyzed coordination polymerization. LLDPE has attracted strong attention in the research of single-site metallocene catalysts and new production technologies. The reason behind this is that LLDPE offers the highest potential for manufacturing of tailor-designed products with improved mechanical performance compared to LDPE [5]. LLDPE is replacing LDPE in certain film applications due to its higher impact strength, tensile strength, and extensibility, which yield films of lower gage but of the same mechanical performance.

2.1.2 Polypropylene

PP is by volume the world's second largest synthetic commodity polymer. It has shown the highest growth rate among all commodity plastics over the past 30 years. Global PP consumption has grown from 1.2 million tons in 1970, to 25 million tons in 1999 and exceeded 36 million tons by 2004. The reasons for the rapid growth in PP applications lie in the great versatility of PP for injected, extruded, and fibrous products [5]. Depending on the stereoregularity of the monomer linkage, PP can be classified into three categories: atactic (random distribution of methyl groups on either side of the chain), isotactic (all methyl groups lie on one side of the chain), and syndiotactic (methyl groups alternate regularly on both sides of the chain) as shown in Figure 2.3.

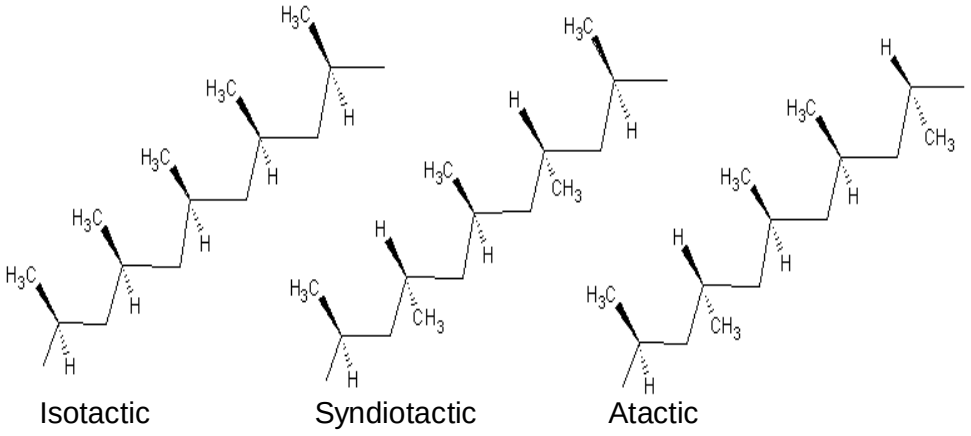


Figure 2.3: Stereoisomers of PP.

All three stereoisomers can be obtained by coordination polymerization. Atactic polypropylene (aPP) was the only form available before the development of stereospecific Ziegler-Natta catalysts. aPP is amorphous and waxy and commercially used as an additive or blended with other polymers. The first industrially important crystalline, high molar mass isotactic PP (iPP) was synthesized by Natta in 1955 using organo-metallic catalysts based on titanium and aluminium [9].

iPP is widely used in injection moulding applications for automotive industry, e.g. in dashboards and bumpers. A high percentage of the overall iPP produced is also used for packaging produced by either blow moulding or thermoforming. Pipes, profiles and films are produced by extrusion. Its high melting temperature (about 165 °C) allows to exploit the properties over a wide temperature range [10,11] and its overall crystallinity, which is related to both stereoregularity and molar mass, promotes some properties such as stiffness, hardness and high-temperature mechanical properties. The application range of iPP has expanded enormously over the last few decades due to blending of iPP with elastomers such as ethylene-propylene copolymers (EP) [12] or ethylene propylene diene terpolymers (EPDM) [13-15], which adds high impact resistance to the resulting polymer.

High impact PP (hiPP) is a two-phase reactor blend, consisting of a semicrystalline matrix phase and a disperse rubber phase. The semicrystalline part is typically iPP and the rubber phase consists of amorphous EP copolymer or EPDM. It is produced in a two-step cascade reactor process: in the first step the semicrystalline matrix is

produced using a Ziegler-Natta catalyst and then the resulting homopolymer is transferred to the second step in which the copolymer phase is produced.

2.1.3 EPDM

EPDM is a terpolymer containing three monomeric units, namely ethylene, propylene and a diene. EPDM is mostly produced using vanadium-based Ziegler-Natta catalysts [16,17]. However, several authors investigated the utilization of metallocene catalysts for EPDM terpoymerization, driven by the desire to overcome low productivity and toxicity of vanadium-based catalysts [16,18,19]. EPDM continues to be one of the most widely used and fastest growing synthetic elastomers having both specialty and general purpose applications. It is by volume the third-largest synthetic elastomer consumed worldwide, after styrene-butadiene and polybutadiene. EPDM elastomers are characterized by an outstanding resistance towards ozone, oxidation, aging, weather and high temperatures [20-22]. These properties can be attributed to the stable and completely saturated polymer backbone structure present in them. Their unique features make EPDM useful for outdoor and elevated temperature applications, such as automotive profiles, single-ply roofing, electrical insulation, belts, window gaskets, and waste-water seals.

Ethylene and propylene are the basic monomers of this polymer and the incorporation of a third monomer (diene) provides unsaturated functionality along the polymer chain which increases vulcanization response by peroxide curing systems or makes the elastomer sulphur curable. Dicyclopentadiene (DCPD), 5-ethylidene-2-norbornene (ENB), 1,4-hexadiene (HD) and vinyl norbornene (VNB) are the dienes typically incorporated in commercial EPDM. Their structures are shown in Figure 2.4.

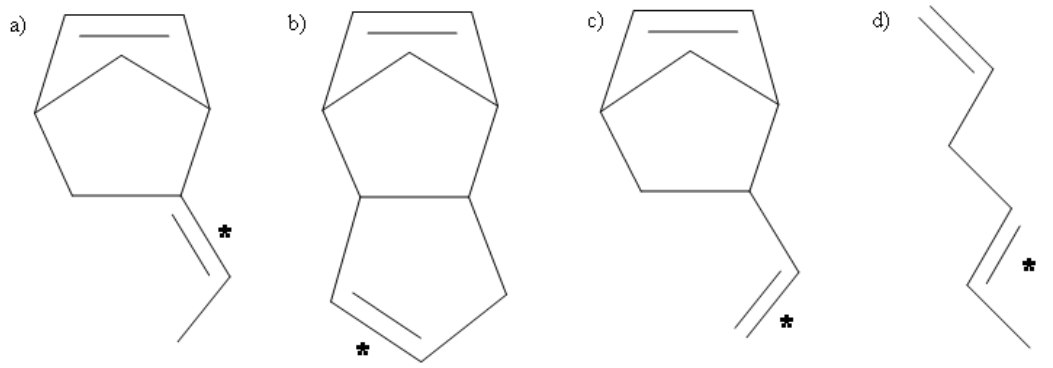


Figure 2.4: Chemical structures of a) ENB b) DCPD c) VNB and HD; the asterisk denotes the double bond which remains unaltered during terpolymerization with ethylene and propylene.

With respect to polymerization, the double bond in the ring is the more reactive one and the other double bond is left as a pendant substituent to the main polymer chain, which is used for crosslinking later. The internal double bond of HD reacts to a small extent during copolymerization, and this is even more so for the cyclopentene double bond of DCPD, resulting in some degree of LCB. The ethylidene unsaturation of ENB hardly reacts and also provides the highest sulphur vulcanization rate. For this reason, HD and DCPD are of minor importance for commercial applications than ENB. Combinations of more than three monomers are occasionally applied. In the main chain of the polymer, the weight ratio of ethylene to propylene varies between 45:55 and 75:25 in industrially produced EPDM elastomers, which leads to glass transition temperatures between -60 ºC and -45 ºC, with some crystallinity for the higher ethylene-containing grades.

3 Characterization of molecular heterogeneity present in synthetic polymers

3.1 Molecular Heterogeneity in polymers

Polymers can display various types of molecular heterogeneities which are interdependent. Each macromolecule is built up of repeating units. The number of monomer units forming a polymer chain is called degree of polymerization (DP). The length of the macromolecules in a given sample may vary, resulting in a molar mass distribution (MMD). Average molar masses can be calculated from the MMD with the most common ones being the weight average molar mass (M_w) and the number average molar mass (M_n). Each polymer chain (except cyclic and branched structures) must also contain two terminal groups. Macromolecules can differ in their architecture, i.e. they can be linear, cyclic or branched (star- or comb-like). In the case of copolymers the composition of the individual macromolecules may vary as well as their composition along the chain, resulting in inter- and intramolecular chemical composition distribution (CCD). Segregation of monomer units along the polymer chain is referred to as the degree of blockiness of the copolymer. The different types of molecular heterogeneity present in a polymer sample are illustrated in Figure 3.1 [23].

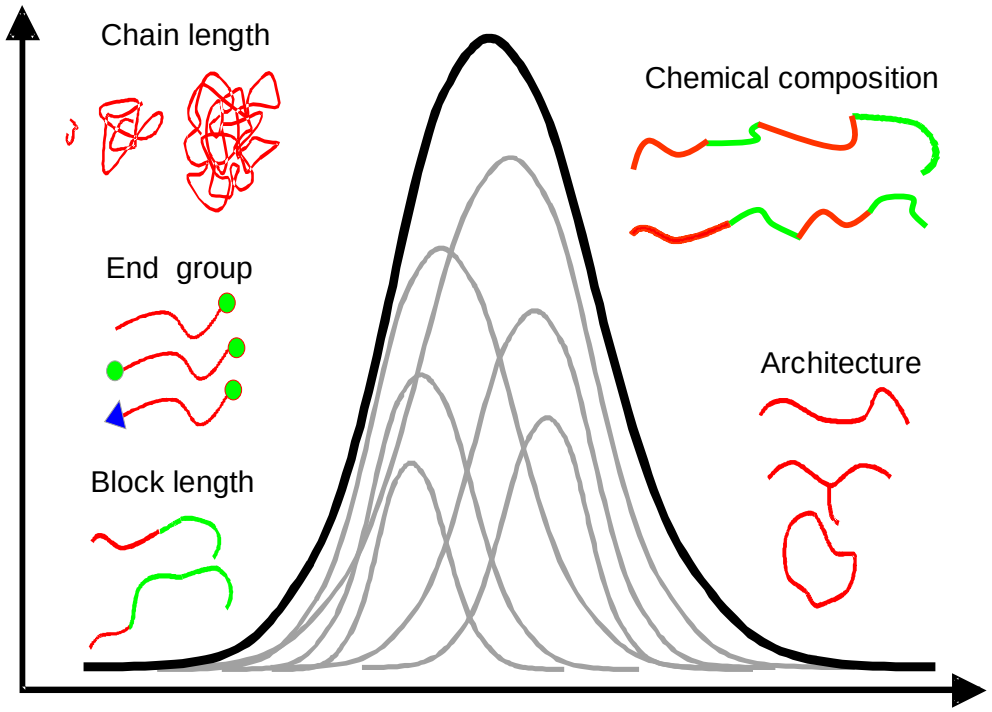


Figure 3.1: Schematic representation of the different molecular heterogeneities occurring in polymers.

Due to their synthesis, synthetic polymers can be heterogeneous with regard to multiple parameters. Measuring these heterogeneities is the key to develop structure↔property relationships, understand reaction mechanisms and kinetics of polymerization, and last but not least to develop processing↔property relationships. To sum up, the end-use properties of polyolefins depend largely on these molecular heterogeneities. Fractionation techniques are used to separate polymer samples according to molar mass, chemical composition, long chain branching or microstructure, which includes the monomer sequence length or stereoregularity [24]. Thus polymer characterization builds a bridge between polymer properties and polymerization conditions [25]. Over the years, increased interest in synthesis of polyolefins with defined structure and tailored properties has led to the demand for accurate, reliable, and convenient methods of measuring microstructure.

3.2 Fractionation techniques based on crystallizability

The chemical heterogeneity present in semicrystalline olefin copolymers can be studied using various techniques. Fractionation techniques like Temperature Rising Elution Fractionation (TREF) or Crystallization Analysis Fractionation (CRYSTAF) are widely used for this purpose. Both techniques separate semicrystalline polyolefins according to differences in their crystallizability.

The fractional crystallization in solution can be explained in terms of the Flory-Huggins theory which relates the depression of the melting or crystallization point to the presence of diluents [26,27]. Non-crystallizing units, comonomer units, and end groups all have an equivalent effect on the depression of the melting point or crystallization temperature when their concentration is low and the units do not enter into the crystal lattice [27]. The reduction of the melting or crystallization point can be related to the content of incorporated diluent.

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V_1}(v_1 - \chi_1 v_1^2) \quad \text{.....(1)}$$

where:

T_m^0 is the melting point of the homopolymer

T_m is the equilibrium melting point of the polymer/diluent mixture

ΔH_u is the heat of fusion per repeating unit

V_u and V_1 are the molar volumes of the polymer repeating unit and the diluent

v_1 is the volume fraction of the diluent

χ_1 is the Flory Huggins thermodynamic interaction parameter

In the case of random copolymers eq. 1 can be reduced to the classical Flory equation (2) [28]:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u}\ln(p) \quad \text{.....(2)}$$

where:

ΔH_u is the heat of fusion per homopolymer repeating unit

p is the molar fraction of the crystallizing unit

Wild et al. established TREF as the analytical technique for the analysis of the CCD [29,30]. In TREF the sample is dissolved in a thermodynamically good solvent at elevated temperature and the solution is then introduced into a column containing a support (e.g. sea sand or glass beads). This is followed by a slow cooling cycle according to a programmed temperature gradient during which the macromolecules are fractionated according to their crystallizability which is related to the composition according to eq. 2. Thereafter the polymer is eluted by adding fresh solvent and simultaneously raising the temperature (heating cycle). TREF can be performed either on an analytical (a-TREF) or preparative (p-TREF) scale. In a-TREF the concentration of the polymer in solution during the heating cycle is monitored using an infrared detector. In the preparative version fractions of the polymer are collected which can later be analyzed by e.g. SEC, NMR or infrared spectroscopy. TREF has been recognized as the most powerful and reliable technique for the structural analysis of LLDPEs and their blends [31,32]. Reviews have been published by Wild [33], Glöckner [34], Monrabal [35,36], Fonseca [37] and Soares [38].

CRYSTAF was developed by Monrabal [27,39] in the early 1990s with the aim to speed up the analysis of the CCD. Unlike TREF, CRYSTAF uses only a cooling cycle for fractionation and thus sample analysis time is reduced. Moreover five samples can be simultaneously analyzed per run, which typically takes between 8 and 24 hours. In CRYSTAF the polymer is dissolved in a solvent at elevated temperature and cooled in a programmed temperature gradient, similar to TREF. During the cooling cycle the concentration of the polymer in solution is measured by an IR-detector. The first derivative of the concentration profile (Wt. %) yields the compositional distribution (dW/dT) as shown in Figure 3.2.

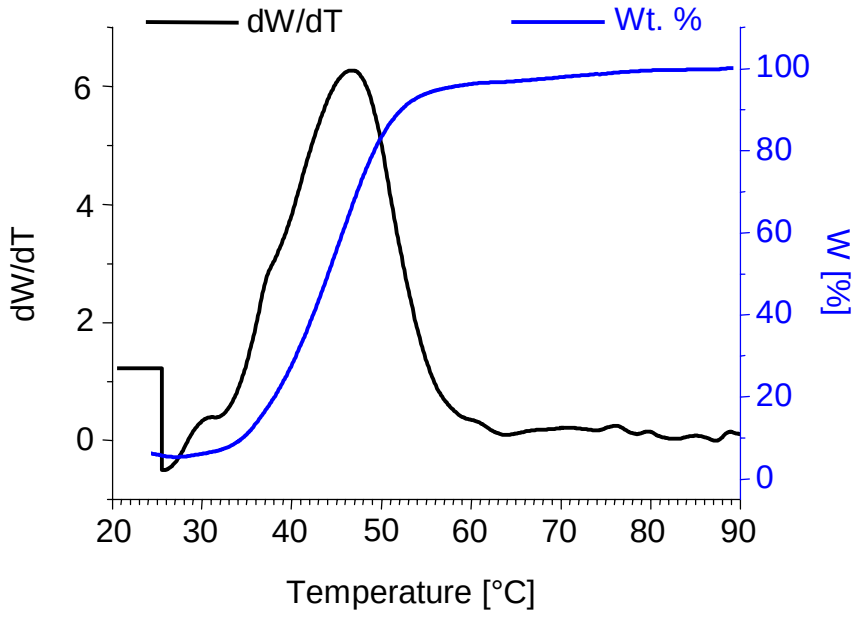


Figure 3.2: Concentration profile (Wt. %) and its first derivative (dW/dT) of a CRYSTAF analysis.

Wt. % above any crystallization provides a straight line corresponding to the initial polymer concentration in solution and resulting in a flat baseline of the differential curve, dW/dT. As the temperature is decreased the polymer will precipitate according to the crystallizability of the individual macromolecules. The last data points of Wt. %, corresponding to the lowest temperature of the crystallization cycle, represent the fraction which has not crystallized and remains in solution, commonly referred to as soluble fraction.

CRYSTAF has been used to determine the CCD in various semicrystalline polyolefins [35,40-43]. Separation of blends of isotactic, syndiotactic and atactic polypropylene and wide variety of ethylene copolymers using CRYSTAF has been reported [41,44-46]. Owing to differences in their crystallinity, the stereoisomers of PP, with the isotactic being the most crystalline and the atactic being amorphous, can be fractionated into the individual components [45]. TREF and CRYSTAF have also been used to characterize the CCD of functionalized polyolefins, EVA, EMA and EBA copolymers [47,48]. Soares [38], Anantawaraskul [49] and Monrabal [36] have reviewed the applications of CRYSTAF.

Recently, a novel characterization technique called Crystallization Elution Fractionation (CEF) has been introduced by Monrabal [50,51] to reduce co-crystallization and improve resolution. CEF involves two fractionation steps: crystallization and elution. This technique is based on a new separation principle referred to as Dynamic Crystallization. It separates fractions inside a column by crystallizability while a slow flow of solvent is passing through the column. As the separation occurs during the crystallization cycle results are comparable to CRYSTAF. CEF combines the separation power of Dynamic Crystallization in the crystallization step with the separation during dissolution of the TREF, consequently the resolution is improved. This new technique has drastically reduced analysis time to under one hour while obtaining the same CCD information. It was shown that CEF is more robust and less prone to co-crystallization than CRYSTAF [52]. However, only a few applications have been demonstrated so far.

All the above mentioned crystallization-based fractionation techniques are not applicable to amorphous polyolefins. Thus the CCD of a wide variety of commercially very important polyolefins, including for example EP, EPDM, and ULDPE, cannot be determined. Additionally, amorphous portions present in a semicrystalline sample, can, however, have a significant impact on the material's performance [53,54]. Moreover, these techniques may not always provide the best solution for complex multi-component resins due to co-crystallization [46,52,55,56] and a narrow working range of comonomer content (samples with comonomer content >10 mol % can not be selectively fractionated) are the other limitations. This makes separation and characterization challenging for many elastomers as they are amorphous at room temperature.

3.3 Chromatographic techniques for the characterization of polymers

High performance liquid chromatography (HPLC) is an important and powerful tool in polymer characterization [57-62]. For many years, HPLC has served as a premier method to characterize complex synthetic polymers, including copolymers, having various types of molecular heterogeneities. Depending on the mechanism three modes of chromatographic separation can be distinguished in the case of polymers (Figure 3.3).

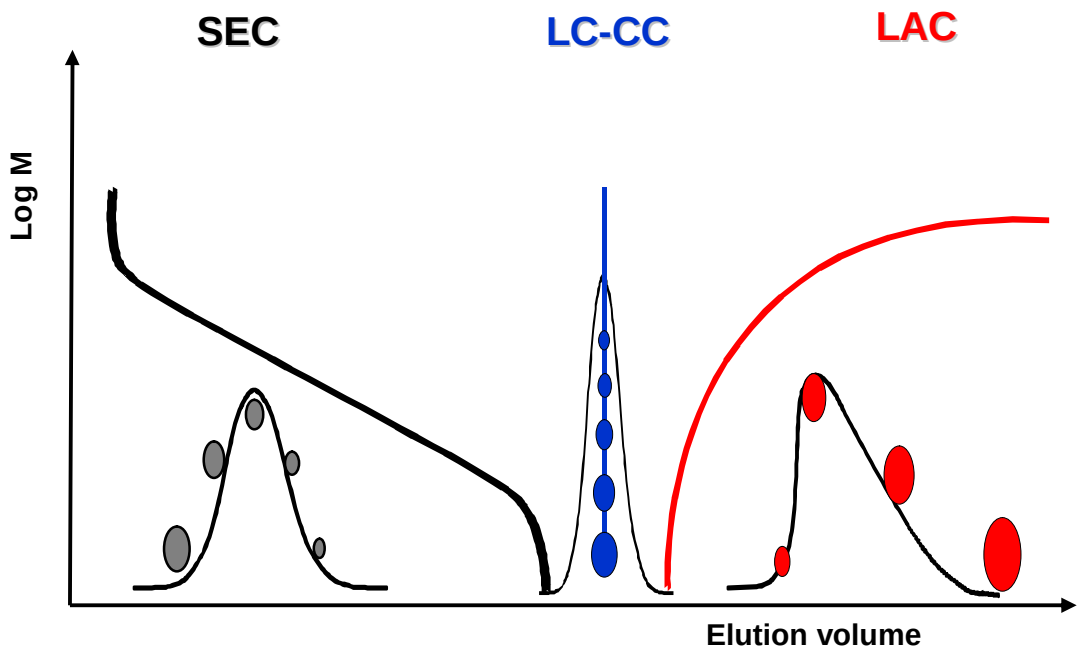


Figure 3.3: Chromatographic behavior with respect to molar mass of a polymer in the three basic chromatographic modes.

In Size Exclusion Chromatography (SEC) the macromolecules are separated with regard to their size in solution (hydrodynamic volume) and the elution volume decreases with increasing molar mass. The separation in SEC is entropy driven [63]. SEC of semicrystalline polyolefins is carried out at temperatures between 130 and 160 °C, which are required to dissolve them in the mobile phase. In liquid adsorption chromatography (LAC) the separation is enthalpy controlled and the elution volume increases with the molar mass of the macromolecule. The chromatographic conditions are designed such that the macromolecules interact with the stationary phase elute according to their chemical composition. In the third chromatographic mode, Liquid Chromatography at Critical Conditions (LCCC), the enthalpic and entropic interactions compensate each other. In LCCC macromolecules of a given homopolymer elute irrespective of their molar mass. These conditions were first identified by Belenky and Tennikov [64-66]. The critical conditions for a given homopolymer vary with temperature, column packing, and mobile phase. LCCC conditions have been experimentally established for more than one hundred HPLC systems [67]. LCCC can for example be used to separate macromolecules according to end groups and/or architecture.

In a chromatographic experiment the complex polymer sample is dissolved in the mobile phase. The solution is then injected into the chromatographic column. The separation in any chromatographic process is related to the selective distribution of the analyte between a mobile phase and a stationary phase of a given chromatographic system [68]. The separation process in liquid chromatography can be described by:

$$\Delta G = \Delta H - T\Delta S = -RT \ln K_d \quad \text{.....(3)}$$

$$\ln K_d = \frac{-\Delta G}{RT} = \frac{-\Delta H + T\Delta S}{RT} \quad \text{.....(4)}$$

where R is the universal gas constant, T is the absolute temperature, ΔH and ΔS are the changes in interaction enthalpy and conformational entropy, respectively and K_d is the distribution coefficient which is equal to the ratio of the analyte concentration in the stationary phase and in the mobile phase.

K_d is related thermodynamically to the free energy difference ΔG of the molecules in the two phases [60]. This difference in free energy comprises of enthalpic (ΔH) and entropic (ΔS) contributions [59]. Experimentally K_d is determined from the following equation:

$$K_d = \frac{V_R - V_i}{V_P} \quad \text{.....(5)}$$

where V_R is the retention volume of the analyte, V_P the pore volume of the stationary phase and V_i the interstitial volume of the column.

When analyzing small molecules the entropic term does not play a significant role in comparison with the enthalpic one describing adsorbing interactions. However, for polymers, the entropic term has to be carefully taken into account since macromolecules are able to undergo large changes in conformation when being in solution or adsorbed to a surface. As it will be described later, the separation mechanism of SEC is governed mainly by entropic contributions.

3.3.1 Size exclusion chromatography (SEC)

SEC is the technique of choice to separate macromolecules according to their molar mass. In ideal SEC, the separation is accomplished exclusively with respect to the hydrodynamic volume of the macromolecules and ΔH by definition is zero i.e., no interaction exists between the stationary phase and the polymer molecules [69]. The distribution coefficient is given by:

$$K_d = K_{SEC} = \exp\left(\frac{\Delta S}{R}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

A macromolecule which enters a pore cannot anymore occupy all possible conformations. This results in a decrease of its conformational entropy. Since the conformational entropy decreases (ΔS<0), the distribution coefficient, $K_{SEC,}$ is <1 in ideal SEC. The larger the macromolecule is, the larger the decrease of the entropy. Thus, macromolecules with the largest volume in the solution are eluted first and elution occurs in the order of decreasing hydrodynamic volume. SEC is not a direct method to obtain the molar mass of the sample. The latter is obtained from a calibration made by using narrow disperse polymer standards (for example, PS or PE) of known average molar masses [57].

The stationary phase consists of a porous material with a defined pore size distribution. The mobile phase should dissolve the polymer properly and avoid interactions between the stationary phase and the macromolecules, i.e. a thermodynamically good solvent is required. Thus, the separation is only directed by entropic contributions [63]. Since SEC separates according to hydrodynamic volume, macromolecules having the same hydrodynamic volume but differing in their chemical composition can not be distinguished by SEC alone. Coupling SEC with spectroscopic techniques, such as FTIR [70,71] or NMR [72,73] enables to determine average chemical compositions along the molar mass axis.

SEC of semicrystalline polyolefins and olefin copolymers is generally carried out at elevated temperatures, which are required to dissolve them in the mobile phase. Generally, a dissolution time between 1-6 hours at a temperature between 150-180

°C is recommended using high boiling solvents like ortho-dichlorobenzene (ODCB) and 1,2,4-trichlorobenzene (TCB) [57]. Various dissolution procedures were described in the literature [74-78].

3.3.2 Liquid Adsorption Chromatography (LAC)

LAC has been widely employed to separate polymers which are soluble at ambient temperatures according to their composition. The separation is driven by adsorptive interactions between the macromolecules and the stationary phase. In LAC conformational changes are assumed to be zero (ΔS=0) because the pores of the stationary phase are sufficiently large to accommodate all macromolecules. The enthalpic contribution (ΔH) is due to attractive interactions of the molecules with the stationary phase. Hence, macromolecules with higher molar mass will be stronger adsorbed on the stationary phase and will elute later than the macromolecules of lower molar mass [79]. The distribution coefficient in adsorptive mode is given by:

$$K_d = K_{LAC} = \exp\frac{(-\Delta H)}{RT} \quad \text{.....(7)}$$

Since ΔH is negative the values of the distribution coefficient K_{LAC} are > 1. In order to achieve enthalpic interactions between the dissolved macromolecules and the stationary phase a thermodynamically poor i.e., adsorption promoting solvent is used as mobile phase. By adding a thermodynamically good (desorption promoting) solvent the enthalpic interactions between the macromolecules and the stationary phase can be overcome, and the macromolecules elute inverse according to their molar mass, i.e. small ones first and large ones later. The reason behind this is that the with increasing molar mass the number of interacting units and consequently the adsorption of the molecules on the stationary phase increases. This phenomenon can be explained by the multiple attachment mechanism proposed by Glöckner [80]. The molar mass dependence in LAC is opposite to that in SEC. The strength of interaction between the analyte molecules and the stationary phase can be either controlled by the eluent composition (e.g. solvent gradient) and/or the temperature [62].

3.3.2.1 LAC of polyolefins

LAC could be an alternative to fractionation techniques like TREF, CRYSTAF or CEF for a fast routine analytical separation of polyolefins and olefin copolymers according to their chemical composition regardless of their crystalline nature. Unless otherwise mentioned the term HPLC (High Temperature High Performance Liquid Chromatography) is synonymously used for LAC in the following due to branding of this term in literature. The efficiency of HT-HPLC (High Temperature High Performance Liquid Chromatography) for the compositional separation of olefin copolymers containing polar comonomers was compared with that of CRYSTAF and TREF by Albrecht et al. [47] who demonstrated that HPLC can be more selective, efficient, and faster. However, the challenge to separate non-polar polyolefins using interactive HPLC is still open. Unlike other polymers which are readily soluble in a variety of solvents at ambient temperature, polyolefins require temperatures > 100 °C to be dissolved due to their semi-crystalline nature which severely limits the choice of solvents potentially suitable as mobile phase. An even larger obstacle is insufficient knowledge about possible stationary phases, which are selective for these non polar polymers and can at the same time withstand high temperatures. All these constraints make it very challenging to identify new sorbent/solvent systems for interactive HPLC of polyolefins.

Several attempts were made to chromatographically separate polyolefins according to their chemical composition. The very first demonstration for the adsorption of linear PE [81-84] or iPP [83-85] onto a column packing material were shown using zeolites as stationary phase. In most of these cases full adsorption of the polymer was found from thermodynamically good solvents for PE, such as TCB, decalin and mesitylene. PE and iPP were either fully or partially retained on the zeolites. It was shown that n-alkanes with C5-C50 carbons are adsorbed when a suitable zeolite and mobile phase were selected. [86-90] An increased retention of some branched alkanes was also found [90]. However, in the case of polyolefins the adsorption on zeolites was irreversible. This was attributed to the narrow pore size in zeolites, which are comparable to the dimensions of macromolecules in their linear conformations. When the pores are fully blocked with adsorbed macromolecules, solvent molecules can not diffuse into pores and displace the adsorbed macromolecules.

The first reversible adsorption and desorption of polyolefins on a chromatographic column was demonstrated by Macko et al. [91]. The separation of PE from iPP in this chromatographic system was based on the fact that iPP, but not linear PE, is soluble in ethylene glycol monobutyl ether (EGMBE) [92]. A substantial improvement in the recovery of the separated PE and PP was achieved by Heinz and Pasch [93] by a solvent gradient EGMBE→TCB. While iPP elutes in SEC-mode in EGMBE, PE is precipitated onto the column and elutes later in the solvent gradient. Although blends of EP-copolymers could be separated according to their composition [94], it turned out that the separation strongly depends on molar mass, which is undesirable in interactive HPLC.

The challenge, therefore, remained to find a suitable sorbent which allows selective and reversible adsorption of polyolefins at high temperatures. The answer to this long standing question of chromatography was the use of carbon-based sorbent. Möckel et al. [95] found that n-alkanes are retained on a carbon-based column (Hypercarb) from methanol stronger than on a reversed phase silica gel. Adsorption isotherm studies by Kalies et al. [96] revealed that n-alkanes are preferentially adsorbed from alcohols on a carbon sorbent. Findenegg and Liphard observed that C_{16}-C_{32} alkanes show affinity towards a graphite surface via adsorption isotherm measurements [97]. Yin et al., also found that there were interactions between graphite and C_8-C_{34} alkanes [98]. Additionally, the strength of interaction increases with the chain length. Considering all these results, it can be hypothesized that PE should show comparable interactions with a graphite surface because n-alkanes are oligomers of PE. This resulted in realization of the first liquid adsorption chromatographic separation of polyolefins [99] on graphitic carbon: A carbon-based stationary phase (Hypercarb) enabled for the first time to fractionate PE and PP by an adsorption and desorption mechanism at 160 °C. Using 1-decanol as mobile phase PP eluted from the Hypercarb column in SEC mode while linear PE, aPP as well as sPP were fully adsorbed. These adsorbed polymers were desorbed only after applying a gradient 1-decanol→TCB. It was shown that this HPLC system enables to separate PE from PP, PP according to tacticity [100,101] and ethylene/1-alkene [102,103] as well as propene/1-alkene copolymers according to comonomer content [104]. It was demonstrated that short chain branching decreases the retention of ethylene/1-alkene copolymers on Hypercarb and the elution volume is indirectly proportional to

the degree of branching. This was attributed to the steric hindrance given by the short chain branches for the orientation of methylene sequence of the polymer backbone in flat conformation on the graphite surface, which enable the most intense van der Wals interactions between the methylene backbone and the graphite surface.

This unique selectivity of Hypercarb spurred interest to probe other commercially available carbon sorbents as well as to test different mobile phases and to elaborate new HPLC systems for separation of various types of polyolefins. The corresponding details represent the content of this PhD-work and will be described later.

3.3.3 Two-dimensional Liquid Chromatography

As the size of a macromolecule in dilute solution is a complex function of different molecular properties such as molar mass, chemical composition, chain stiffness and architecture (i.e. topology and microstructure), selective separations of macromolecules with regard to these parameters are needed [105]. MMD and CCD are the two basic molecular parameters which are of interest in industrial polyolefins, as they decisively impact the properties of the final products. Even though, the individual parameters can be studied separately by HPLC and SEC the relationship between MMD and CCD can only be obtained by coupling the two chromatography modes in 2-dimensional LC (2D-LC). This procedure was first applied for analytical characterization of synthetic polymers by Balke in 1982 [106] and later elaborated by Pasch [59,107,108], Kilz [109,110] and others [111-114].

Two-dimensional chromatography involves off-line [60,112,115-118] or on-line [119,120] collection of eluent fractions from the first chromatographic separation (D1) followed by re-injection of the individual fractions into the second chromatographic system (D2). However, the off-line approach has difficulty obtaining a sufficient number of fractions to represent the elution profile of the D1 chromatographic separation. This drawback is overcome by on-line coupling, giving rise to comprehensive two-dimensional liquid chromatography [121]. Hence the on-line or automated two-dimensional systems have gained popularity in recent years. Figure 3.4 shows the scheme of an on-line two-dimensional liquid chromatographic system.

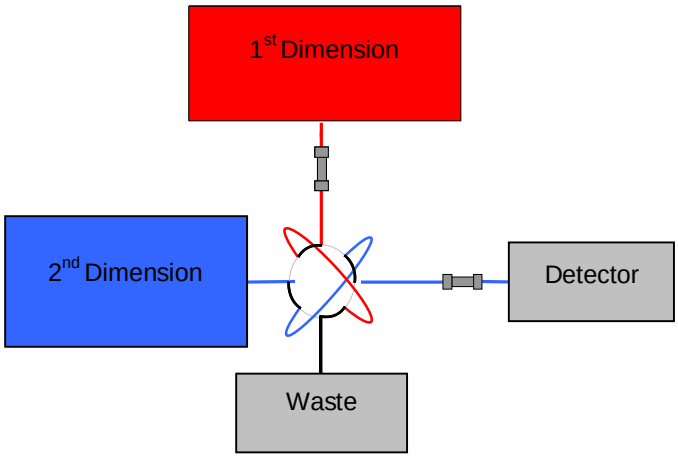


Figure 3.4: Schematic representation of a 2D-LC system, in red the first dimension route (D1), in blue the second dimension route (D2).

The coupling between the two dimensions is achieved via a switching valve equipped with two loops. As one of them is collecting the eluent from the D1 column, the sample having been collected in the other loop is injected into the D2 column. The separation in D2 needs to be complete within the time window defined by the ratio of the volume collected in sample loop divided by the flow rate of D1 [111]. To represent a continuous distribution, a large number of fractions from the D1 separation, each with a small volume, is desired. High speed in the D2 separation is thus mandatory in order to provide for timely analysis.

Using HPLC as D1 and SEC as D2 (HPLC x SEC) has been widely practiced [122-124], whereas the studies of comprehensive 2D LC by SEC x HPLC were seldom reported [125]. The popularity of the former configuration is due to the fact that SEC can be easily sped up. Parameters, such as column length, flow rate, and temperature, were investigated with the goal to achieve good resolution at high speed [114,126,127]. An additional advantage is that multiple detectors can be used in the HPLC x SEC configuration, but not in the SEC x HPLC case. However, such separations were realized at high temperature only recently for functionalized semicrystalline polyolefins [128], ethylene/1-octene copolymers [129], and polyolefin blends [130,131]. Polymer samples undergo two fractionation steps in 2D LC, finally

resulting in highly diluted analytes. Highly sensitive detectors are thus required for quantification.

The advantages and disadvantages of using either HPLC x SEC or SEC x HPLC sequences were discussed in detail by van der Host and Schoenmakers [121,132]. A number of reviews have been published to better understand the issues of 2D LC [133-135] and also how to optimize 2D LC by choosing the best suited chromatographic systems with regard to the desired information [132].

3.4 Carbon sorbents for HT-HPLC of polyolefins

A number of carbon sorbents are commercially available and some varieties of carbon are industrially produced even on a large scale [136]. Carbon sorbents are widely used in filtration processes, and it is state of the art in pulp, paper, and petroleum industries to remove environmentally hazardous chemicals from waste waters by using graphitized carbon black (GCB) or porous graphitic carbon [137]. GCB filters can be employed to capture undesirable chemicals from drinking water [138,139]. Environmental analysts used graphitic carbon in solid phase extraction cartridges for sample preconcentration and cleanup[140]. Since the pioneering work of Kiselev and co-workers [141,142], carbon sorbents have been increasingly applied in gas and liquid chromatography. However, in most cases these supports had serious drawbacks like poor mechanical stability, low surface area available for interactions, lack of energetically homogeneous surface, and non-uniform pore structure which limited their applications in liquid chromatography (LC). The first attempt to prepare a carbonaceous sorbent suitable for LC was made by Guiochon and co-workers [143]. To meet the requirements of LC various procedures for the preparation of carbon sorbents were proposed [136,144-153] and their adsorption properties were studied [95,154-158].

Carbon supports are sufficiently different from other reversed phase supports to be of interest to the chromatographic community. They are commonly more retentive towards polar compounds and are often more selective for the separation of isomers and homologues than bonded phases. They also exhibit greater chemical stability

over a wider range of pH and temperature than the bonded phases. [159-161]. Leboda and Knox reviewed applications of various carbon sorbents in LC [162,163].

3.4.1 Hypercarb

Hypercarb is a porous graphitic carbon which was first applied in HPLC and gas chromatography (GC) by Gilbert and Knox [136,146]. It is produced in several steps:

1) A highly porous silica material is used as template for the carbon based material and impregnated with a phenol-formaldehyde mixture.

2) This mixture is polymerised to produce a phenol-formaldehyde resin.

3) This material is then carbonised by heating to approximately 1000 °C in nitrogen to yield solid particles consisting of a silica backbone with carbon filled pores.

4) The silica backbone is then removed by dissolution in 5M sodium hydroxide solution.

5) By heating the material above 2000 °C, a complete rearrangement of the carbon structure results, changing the material from a microporous amorphous structure to a crystalline material with a planar surface. The resulting material was called “porous graphitized carbon” (PGC). The material is now marketed under the trade name Hypercarb.

Particles of PGC are spherical and fully porous. The surface of PGC is crystalline and does not contain micropores. The internal surface of PGC comprises flat sheets of hexagonally arranged carbon atoms comparable to a very large polynuclear aromatic hydrocarbon molecule [164]. Figure 3.5 shows a schematic representation and a scanning tunneling microscopy image of graphite on which n-decane is adsorbed with its carbon skeleton parallel to the graphite surface plane.

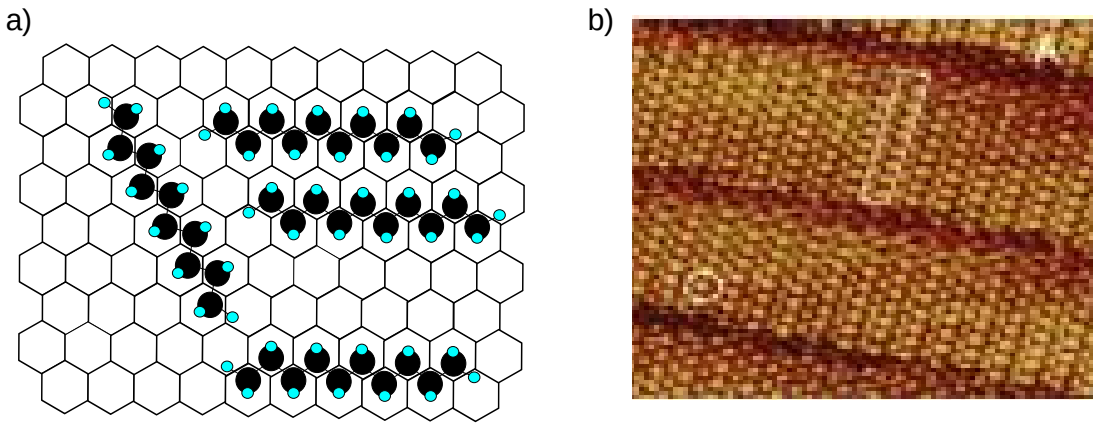


Figure 3.5: a) Schematic representation and b) Scanning tunneling microscopy image of graphite with monolayer structures of n-decane [165].

There are, in principle, no adventitious functional groups on the surface. The individual sheets of carbon atoms are held together by London dispersion interactions (i.e., instantaneous dipole-induced dipoles between the carbon atoms in adjacent sheets).

PGC behaves primarily as a strong reversed-phase stationary phase. However, due to its flat and highly crystalline surface and the aromatic nature the mechanism of interaction is very different from that of conventional silica based reversed phases [164]. The aromatic system of the graphite can interact with non-polar analytes due to dispersive interactions as well as with polar ones via induced dipoles. Increasing the hydrophobicity of an analyte by adding CH_2-groups increases retention. Analytes having lone-pairs [166] or π-electrons [167] can also interact with PGC surface via electron transfer. Hence, the nature of the interactions between the analytes and the carbon is rather complex. The strength of interaction depends on both the molecular area of an analyte (and, therefore its shape) in contact with the graphite surface and upon the nature and type of functional groups at the point of interactions with the flat graphite surface. The more planar an analyte, the more retention it shows on the flat, crystalline PGC surface due to its closer alignment to the graphite surface, which leads to greater number of points of interactions. However, the flatness of the surface reduces retention of highly structured and rigid molecules which can contact the graphite surface only through a small part of their surface, compared with planar

molecules having the same molecular mass. This is illustrated in Figure 3.6. Molecular size will only confer strong retention when the molecule is very flexible and can adapt to the flat surface.

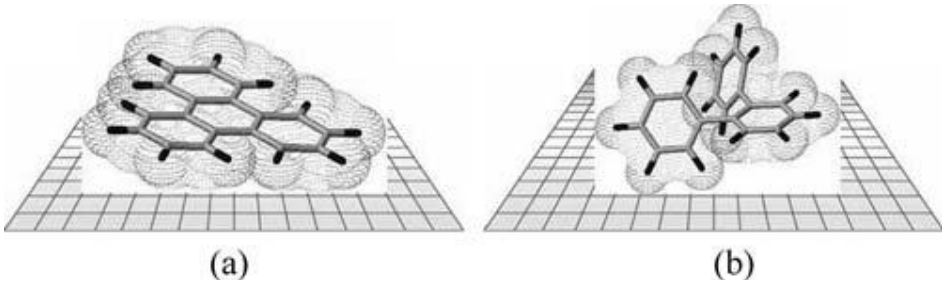


Figure 3.6: Effect of the solute shape on the strength of the interaction with the graphite surface: a) Good alignment of planar molecule to the flat graphite surface; b) Poor alignment of non-planar molecule to the flat graphite surface [168].

PGC has proven to be unique in chromatographic separation. Several studies indicate that PGC is superior to silica-based reversed phases, because it shows selectivity toward particular structural features in molecules such as alkyl chains or isomeric structures [95,136,154,157]. These studies reveal that the flat rigid surface structure provides good stereoselective discrimination, especially in the case of geometric isomers and some diastereomers. Tanaka et al. [154] observed that when changing from alkanes to their corresponding alkanols, the retention was substantially reduced on octadecylsilane (ODS). However, on PGC the retention was larger for the alkanols.

This feature of PGC is attributed to the flat graphite surface, which allows for stronger dispersive interactions with those molecules which can align themselves better to the flat surface.

Coquart and Hennion highlighted the polar retention effect in their study of trace level determination of polar phenolic compounds in aqueous samples [169]. Their results showed that by increasing the hydroxyl substitution on the benzene ring, the retention was decreased substantially, often leading to the analytes being unretained on ODS. Conversely, increasing the number of hydroxyl functionalities on the aromatic ring increased the retention significantly on PGC. Wan and co-workers

studied the retention of 36 positional isomers of substituted benzenes on PGC and C18-silica and confirmed the superior steric selectivity of PGC [170]. Forgács and co-workers carried out extensive studies on the retention of various classes of compounds such as phenol, aniline and barbituric acid derivatives by PGC [171-175] and found that more polar or hydrophilic analytes are retained stronger and eluted later. The retention behavior of poly ethoxylated alcohols on PGC and C18-silica was studied by Chaimbault et al. [166]. In detail it was shown that the retention on PGC increased with both, the length of the hydrocarbon chain and the number of ethylene oxide units. PGC showed a stronger retention for equivalent compounds than C18 silica. Henion et al. [176] analyzed the solute polarity and concluded that retention factor increases with the number of polar substituents on the aromatic ring. Jackson and Carr showed that any polar functional group attached to the benzene ring induces an increase in retention, regardless of its electron-donor or electron-acceptor properties [177]. This behavior was explained by the polarizability of the carbon surface due to the overlapping of the hybridized orbitals, allowing dipole type and electron lone pair donor-acceptor interactions.

Kaliszan and co-workers [178] demonstrated using quantitative structure-retention relationships that PGC behaves primarily as an electron pair acceptor for substituted aromatic solutes capable of electron donation under non-polar solvent conditions. These and other studies provided strong evidence that retention on PGC was in many cases quite unlike that for any other reversed phase support.

3.4.2 ZirChrom-CARB

Carbon-clad zirconia (C/ZrO_2, ZirChrom-CARB) is another carbon based sorbent which has been successfully applied in LC. Zirconia (ZrO_2), which acts as a support, consists of crystalline, colloidal material, aggregated by polymer-induced colloid aggregation to form monodisperse, chromatographically useful spherical particles [179]. Porous zirconica particles have shown no signs of dissolution over the entire pH range and have been used for prolonged periods in chromatographic separations at temperatures up to 200 °C. Extreme robustness, stability and high porosity of these particles have lead to the application of zirconia-based columns in chromatographic separations [179-182]. Various zirconia-based HPLC phases are

also commercially available and encompass many of the most frequently used chromatography modes.

ZirChrom-CARB has been developed and manufactured by Zirchrom Separations, Inc. It is prepared by chemical vapour deposition (CVD) of carbon on a porous ZrO_2 microspherule support at temperatures up to 700 °C by passing volatile organic vapours at reduced pressure [151,152,183-185]. Vapour sources used for deposition include heptane, isooctane, cyclopentane, 1-butanol, toluene and 1,7-octadiene. After completion of the deposition process, the carbon-coated particles were Soxhlet extracted with either tetrahydrofuran or heptane. This procedure yields a mechanically and chemically stable material which combines the advantages of the inorganic support, zirconia (mechanical stability, well-controlled pore structure, and high surface area), with those of carbon-based sorbents (chemical stability and unique chromatographic selectivity). Physical and chemical properties of ZirChrom-CARB were extensively explored [151,152,177,183,185,186] showing that it retains the unique selectivity of carbon materials and serves as a reversed phase support for LC but with enhanced mechanical stability. The quality of C/ZrO_2 chromatographic supports obtained by CVD highly depends on the source of carbon used for the CVD [183]. In particular, when a saturated hydrocarbon is used as the carbon source the chromatographic efficiency and loading capacity of the support material are much greater than those of supports made by CVD of unsaturated hydrocarbons. This is due to the lower reactivity of the saturated hydrocarbons which increases the probability of molecules diffusing into the porous ZrO_2 particle and decomposing inside the pores. This yields improved energetic homogeneity of the carbon surface.

The chromatographic behavior of carbon-clad zirconia was reported in several works. Fundamental studies comparing the selectivity of ZirChrom-CARB and Hypercarb to conventional reversed-phases have shown that the retention and separation mechanisms of both carbon phases are different from those of aliphatic bonded reversed-phase materials [185]. ZirChrom-CARB, similar to Hypercarb, is more retentive to polar analytes [177,181,185] due to electronic and dipolar interactions and resolves the isomer mixtures [151,183,186] to a greater extent than an ODS based column. The superior selectivity of ZirChrom-CARB for isomers over that of conventional C-18 columns was attributed to the difference in separation mechanism.

Unlike on the C-18 columns, where separation takes place by a partition-like process involving a dynamic surface that is not as sensitive to solute shape, it is adsorption on the carbon surface which takes place when using ZirChrom-CARB [183]. The rigid structure of C/ZrO_2 also makes it more sensitive to solute shape. Consequently, the rigid and polarizable carbon surface is sensitive to the geometric orientation of analytes and leads to chromatographic resolution. For example, in the case of diastereomers, each form has a unique shape and presents a different map of electron density to the carbon phase. Hence the probability of the molecules to localize near the carbon surface varies with the conformation leading to different extents of interaction [186]. In that way carbon based sorbents provide excellent resolving power for stereoisomers. Investigations revealed many chromatographic similarities between carbon-coated zirconia and PGC even though their manufacturing processes are different [177,183,185].

3.4.3 Activated carbon

Activated carbon was one of the first materials used to extract medium- to low-polarity organic compounds from water [187]. It is used for example in waste water treatment, air and gas purification, prevention of gasoline vapour emissions from automobiles and in gas masks [188]. Activated carbon is made from wood, coke, charcoal, or synthetic polymers by pyrolysis [189]. Adsorbent carbons are usually produced by a two-step process of carbonization and then activated by partial gasification. The highly porous structure produced during activation provides an extensive surface area. Activated carbon has a very complex surface structure containing a wide range of functional groups like phenolic, carboxylic, carbonylic, aldehydic, etheric, peroxidic, quinine and lactone groups [190,191]. Acting as polar sorbent with hydrophilic nature the adsorption properties depend on the origin of the raw material and the temperature and atmosphere used during production [191]. The principal binding mechanisms include hydrophobic interactions, charge-transfer complexation, hydrogen bonding and cation exchange.

Very few chromatographic applications of activated carbon were presented in the literature[192-194]. The analyses of polychlorinated dibenzo-p-dioxins and polychlorinated biphenyls present in ash from industrial incinerators and biological

samples were carried out by LC on activated carbon columns [194]. Adsorption isotherm studies indicate that activated carbon adsorbs long chain n-alkanes preferentially than alcohols as a result of higher dispersion forces [96,195]. However, large variations in the physical and chemical properties of the different sources of carbon and strong adsorption of many organic compounds with functional groups limit the application of activated carbon in liquid chromatography.

3.4.4 Exfoliated graphite

Exfoliated graphite, also called thermally expanded graphite, has a low density and a large surface area. It is industrially produced from flaky graphite by intercalation and heat treatments in which the graphite expands up to a couple of hundreds of times in volume, resulting in a puffed-up material with a very low density [196]. This material has a large adsorption capacity to oil and adsorbs more than 80 times of its weight. This feature can be attributed to both, the hydrophobic nature of its surface and the pore structure which facilitates the capillary pumping of oil [197]. Exfoliated graphite is used to recover oil from the surface of water to protect pollution in case of oil spills [198]. The oil sorption capacity of exfoliated graphite increases as its surface area increases and its bulk density decreases.

However, the application of exfoliated graphite in chromatographic separation has not been much explored. Exfoliated graphite can be used as an adsorbent in GC to separate geometrical and structural isomers. Its properties in GC are close to those of GCB. [199]. The only liquid chromatographic separation demonstrated using exfoliated graphite in the literature is the separation of polychlorinated dibenzo-p-dioxins from polychlorinated biphenyls [200].

3.5 Solvents for chromatography of polyolefins

For HPLC of polymers it is a prerequisite to know the solubility of the macromolecules in the corresponding sample solvent or mobile phase of the chromatographic system at the specific temperature. Polyolefins require temperatures of 130 - 160 °C to dissolve due to their semi-crystalline nature. The

solubility of PE or iPP in single solvents was presented [63,201-205]. However, the choice of the solvents is limited by their boiling points. Cloud point indicates the temperature at which the dissolved polymer is no longer completely soluble in a given solvent or the volume fraction of non-solvent which precipitates the polymer from its solution at a given constant temperature. Knowledge of the cloud point of polymers in a solvent can be used for realize and interpret chromatographic separations. Bartkowiak et al. measured cloud points of polymers in various mobile phases and the data was also used to identify the principle of chromatographic separation [206-208]. Macko et al. [209] used a specifically designed apparatus to measure the cloud points of polyolefins in mixed and single solvents. It was shown that a variety of polar solvents, chlorinated solvents and combinations of specific good solvents and non-solvents can be used to dissolve PE and PP at high temperatures. This data was later used in chromatographic method development [85,100,209] as well as in this work.

4 Results and Discussion

4.1 Screening of carbonaceous sorbents and solvents for HT-HPLC of polyolefins – I

4.1.1 Aim of the study

A prerequisite to separate polyolefins with regard to their chemical composition by HPLC is to identify suitable combinations of mobile phase and sorbents (stationary phase) which can provide reversible adsorption of the macromolecules. However, the choice of the solvents which can potentially dissolve semi-crystalline polyolefins at higher temperatures (> 100 °C) and the knowledge of solute interactions with the sorbent and solvents are limited for polyolefins.

A carbon-based stationary phase (Hypercarb) enabled for the first time to fractionate PE and PP by a mechanism of adsorption and desorption [99]. Using 1-decanol as mobile phase iPP eluted from the Hypercarb column in SEC mode, while linear PE, aPP as well as syndiotactic PP (sPP) were fully adsorbed.

With the aim to identify new sorbent/solvent systems for HPLC of polyolefins several mobile and stationary phases were tested. Considering the ability of Hypercarb to fractionate PP, PE and propene/1-alkene copolymers [99,104], two additional carbon based sorbents, namely Zirchrom-CARB and activated carbon TA 95 were tested along with Hypercarb in combination with several polar solvents as mobile phase. The elution behavior of linear PE and isotactic, atactic and syndiotactic PP is described below.

4.1.2 Solubility of PE and PP standards

Complete dissolution of the polymer molecules in the sample solvent and mobile phase is important for liquid adsorption chromatographic separation and also to avoid any blockage in the chromatographic system in frits, capillaries or detector cells

during analysis. The cloud point of polymers gives information about the solvation properties of the solvent. To measure cloud points of PE and PP a specially designed apparatus was used [209]. The polymer was dissolved in the respective solvent at a concentration of 1 mg/mL and the dissolution temperature was 160 °C or adjusted accordingly in the case of solvents with lower boiling points. Transparency of the solution was continuously monitored while the temperature was gradually lowered. A detailed description of the procedure can be found in the experimental section (Chapter 5). Table 4.1a and b summarize the cloud point of PE and PP standards in the respective solvents. When the cloud point data of the polymer can not be collected, its solubility at chromatographic temperature is given in the table.

Table 4.1a: Cloud points of PE (M_w - 260 kg/mol) at 1 mg/mL.

Solvent	**cloud point temperature [°C]**
2-ethyl-1-hexanol	150.5
1-decanol	138
hexylacetate	109
cyclohexylacetate	104
cyclohexanone	133
n-decane	91
EGMBE	Not soluble at 165

Table 4.1b: Cloud points of iPP (M_w **-** 136 kg/mol), aPP (M_w **-** 315 kg/mol) and sPP (M_w **-** 196 kg/mol) at 1 mg/mL.

Polymer / **Solvent**	**Cloud point temperature/solubility at chromatographic temperature [°C]**		
	iPP	**aPP**	**sPP**
2-ethyl-1-hexanol	137	Soluble at 160	Soluble at 160
1-decanol	109	Soluble at 160	Soluble at 160
hexylacetate	100	Soluble at 150	Soluble at 150
cyclohexylacetate	83	Soluble at 160	Soluble at 160
cyclohexanone	94	Soluble at 140	Soluble at 140
n-decane	62	Soluble at 140	Soluble at 140
EGMBE	144.5	Not soluble at 165	Not soluble at 165

All the tested solvents were able to dissolve both PE and PP, except EGMBE, in which only iPP is soluble. It can be seen from the cloud point temperatures that a higher temperature is needed to dissolve PE or PP in solvents with high polarity.

4.1.3 Elution behavior of PE and PP on carbon-based sorbents

The polymer samples were dissolved in the respective mobile phase and injected into the chromatographic column packed with the respective carbon sorbent and in addition also into a capillary (i.e. without column). The peak areas of the detector signal of the respective polymer obtained with the column and those without the column were compared to classify the extent of adsorption of the polymer sample onto the sorbent in a semi quantitative way. In the selected sorbent-solvent systems the adsorbed polymer was desorbed by a linear gradient starting with the polar solvent and ending with pure TCB. It is supposed that the adsorbed polymers were fully desorbed by TCB, because a repeated desorption with TCB did not generate any peak on chromatogram and the measurements were reproducible in long period of time. The tested sorbent-solvent systems and the corresponding elution behavior of PP and PE standards are summarized in Table 4.2.

4.1.3.1 Elution behavior on Zir-Chrom CARB

Figure 4.1 shows the chromatograms of PE and PP eluted isocratic in 2-ethyl-1-hexanol from ZirChrom-CARB.

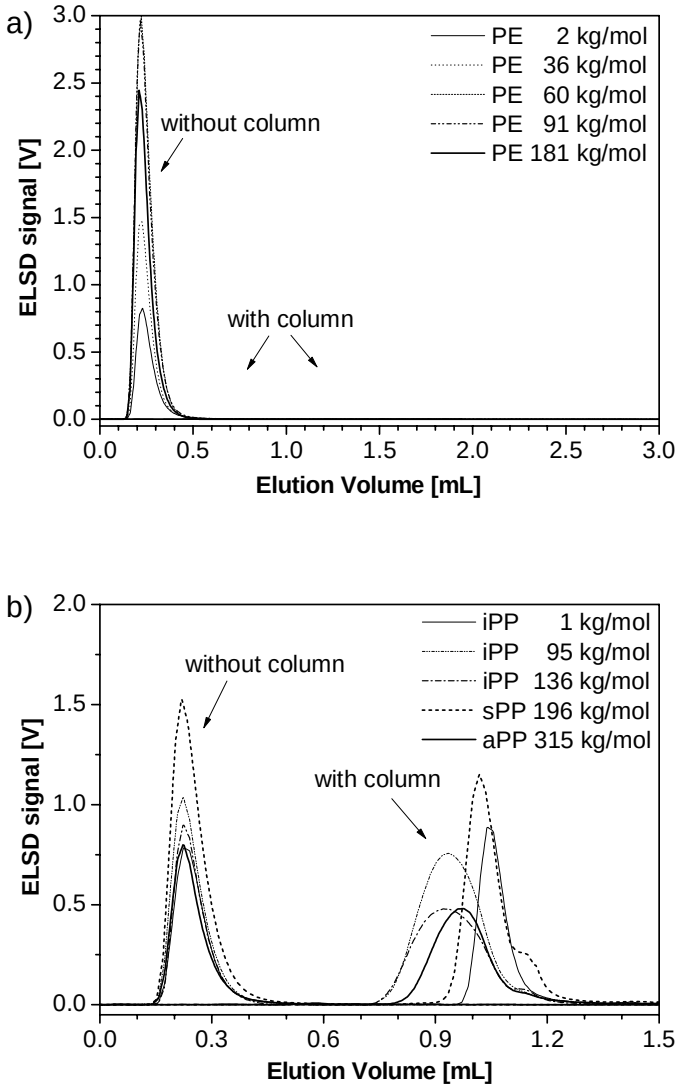


Figure 4.1: Overlay of chromatograms illustrating a) full retention of PE standards and b) elution of PP standards. Sorbent: ZirChrom-CARB. Mobile phase: 2-ethyl-1-hexanol. Temperature: 160 °C. Chromatograph: PL XT-220.

While PE is fully retained (i.e., no peaks appeared on chromatograms as shown in Figure 4.1a), all stereoisomers of PP are not adsorbed and elute in SEC mode (Figure 4.1b). However, the molar mass separation in this column packing is quite poor due to the small pore volume (0.2 mL) of the sorbent and the narrow pore size distribution of the sorbent particles, which is a prerequisite for HPLC columns. As a result, the difference in elution volume between the sample with the highest and lowest molar mass is small, only about 0.2 mL.

In Hypercarb/1-decanol [99] only iPP elutes in SEC mode, while sPP, aPP and PE are fully retained and elute only after the application of a linear gradient 1-decanol→TCB. The elution behavior of PE and PP is tested using ZirChrom-CARB under the same conditions. The results are summarized in Table 4.2. Like with the previous system (Figure 4.1) PP elutes in SEC mode in ZirChrom-CARB/1-decanol and no influence of the stereoregularity of PP on the elution is observed, while PE is retained on the column. The retained PE can be eluted by a gradient 1-decanol→TCB. The chromatograms obtained in the gradient elution of PE are shown in Figure 4.2.

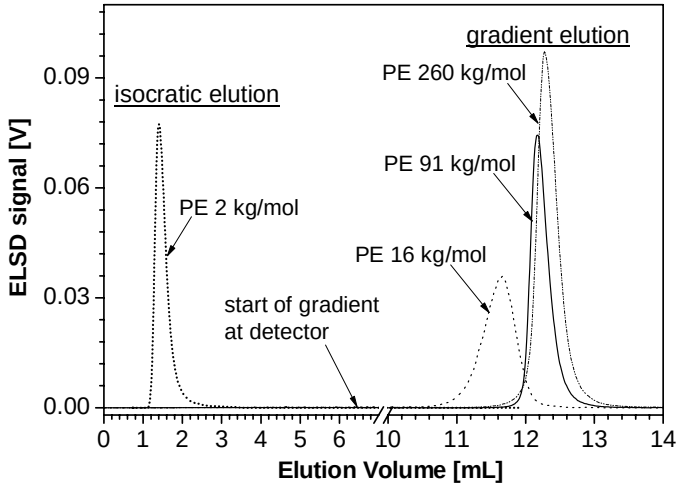


Figure 4.2: Overlay of chromatograms illustrating the elution behavior of PE standards with different molar mass. Sorbent: ZirChrom-CARB. Mobile phase: 1-decanol and gradient 1-decanol→TCB. Temperature: 160 °C. Start of the gradient at pump is indicated in the figure. Chromatograph: PL-GPC 210.

PE with 2 kg/mol is not retained in ZirChrom-CARB/1-decanol, while PE standards of higher molar mass are fully retained (Figure 4.2).The elution volumes of PE with M_w > 16 kg/mol are almost identical. This indicates that the separation is governed mainly by the chemical nature of the polymer (PE contra PP) and the molar mass of the samples plays a secondary role, mainly in the low molar mass region. Full retention of PE and elution of PP is also found from n-hexylacetate or cyclohexylacetate on ZirChrom-CARB (Table 4.2).

Blends of PE and PP standards were injected into ZirChrom-CARB using a gradient 2-ethyl-1-hexanol→TCB, as this chromatographic system shows contrast elution behavior for them. The obtained chromatograms are shown in Figure 4.3.

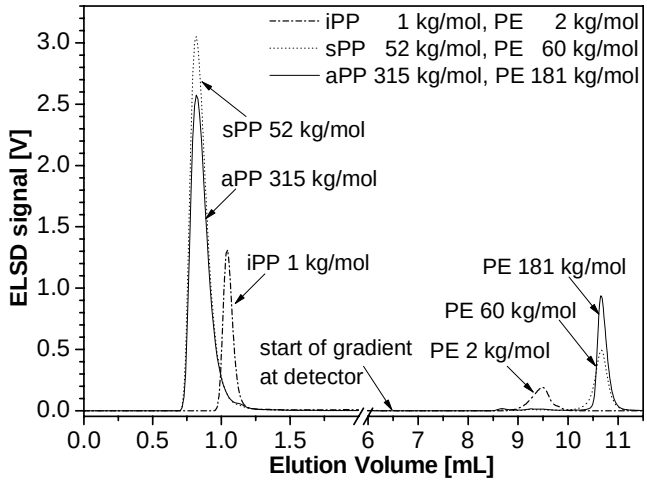


Figure 4.3: Overlay of chromatograms of blends of PE and PP with different molar mass. Sorbent: ZirChrom-CARB. Mobile phase: 2-ethyl-1-hexanol and gradient 2-ethyl-1-hexanol→TCB. Temperature: 160 °C. Start of gradient in pump is shown in the figure. Chromatograph: PL XT- 220.

As shown in Figure 4.3, PE with a wide range of average molar mass is perfectly baseline separated from PP. All PP standards elute in SEC mode (i.e., iPP 1 kg/mol elutes after sPP 52 kg/mol and aPP 315 kg/mol; both PP with higher molar mass are excluded from the pores of the column packing), however the difference between their elution volumes is very small. PE standards elute only after starting the solvent gradient. This chromatographic system separates also PE < 20 kg/mol from PP, which was not possible using the HPLC systems from [91,93]. The application of this chromatographic system is extended to separation of ethylene/1-hexene copolymers with different comonomer content, as PE is completely retained (Figure 4.4).

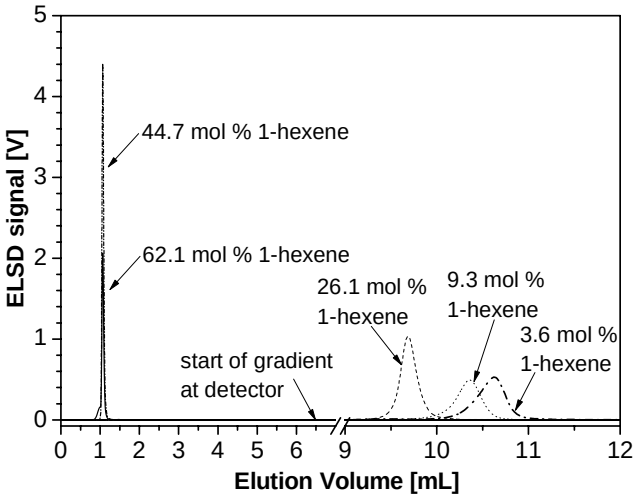


Figure 4.4: Overlay of chromatograms of random ethylene/1-hexene copolymers. Sorbent: ZirChrom-CARB. Mobile phase: 2-ethyl-1-hexanol and gradient 2-ethyl-1-hexanol→TCB. Temperature: 160 °C. Start of gradient in pump is shown in the figure. Chromatograph: PL XT-220.

With increasing 1-hexene content the elution volume at peak maximum decreases. Those samples with low comonomer content are well separated, however the samples with a higher content of 1-hexene are not retained and elute before the gradient i.e., without adsorption. It is assumed that the high content of branches hinders the interaction of the ethylene sequences with the sorbent surface and consequently the polymer is less retained or not retained anymore.

4.1.3.2 Elution behavior on activated carbon TA 95

The elution behavior of PE on TA 95 using 2-ethyl-1-hexanol isocratically is shown in Figure 4.5.

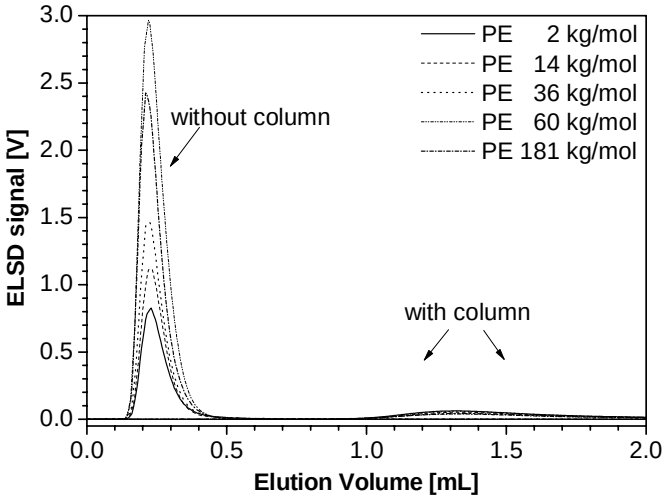


Figure 4.5: Overlay of chromatograms illustrating partial retention of PE standards. Sorbent: TA 95. Mobile phase: 2-ethyl-1-hexanol. Temperature: 160 °C. Chromatograph: PL XT-220.

All PE standards are partially retained, irrespective of their molar mass, as can be recognized by comparing the peak areas obtained with the column with those obtained without the column. Differing from the elution on Hypercarb and ZirChrom-CARB both PE and PP are partially retained on TA 95 from 2-ethyl-1-hexanol.

Figure 4.6 illustrates the elution of PE on TA 95 using a solvent gradient 1-decanol→TCB.

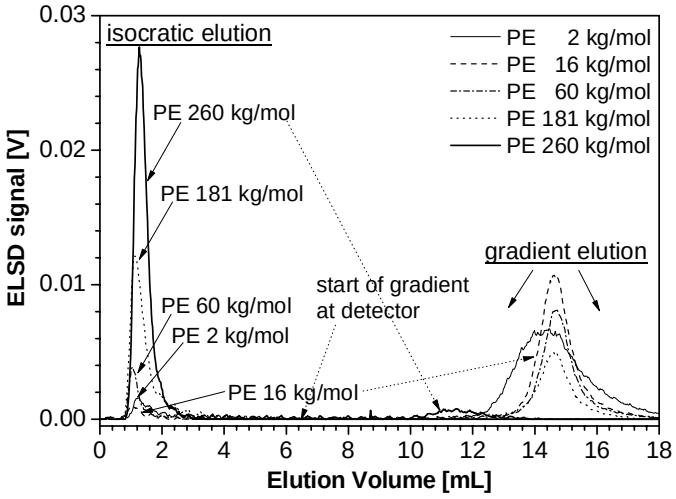


Figure 4.6: Overlay of chromatograms of PE standards Sorbent: TA 95. Mobile phase: 1-decanol and gradient 1-decanol→TCB. Temperature: 160 °C. Start of gradient at detector is shown in the figure. Chromatograph: PL-GPC 210.

For all standards one portion elutes in 1-decanol (i.e., is not retained in TA 95) and the other part elutes only after starting the gradient 1-decanol→TCB. Comparing the peak areas in Figure 4.6 indicates that PE standards with lower molar mass are adsorbed to a larger extent than the higher molar mass ones. This effect for PE and PP was also found in the system TA 95/cyclohexylacetate. As the pores in TA 95 are very small (8 Å), it can be expected that their accessibility for polymers with higher molar mass is limited, which influences the extent of their interaction with the sorbent. Moreover, TA 95 contains polar groups [195], which are not present in both Hypercarb and Zir-Chrom CARB. We suppose that due to these features of the TA 95 PE and PP are either pronouncedly retained (Figure 4.5, 2-ethyl-1-hexanol) or the extent of the polymer adsorption decreases with increasing molar mass (Figure 4.6, 1-decanol) depending on the mobile phase used. Interestingly the elution of PP does not depend on its tacticity like observed in Hypercarb/1-decanol. iPP elutes without adsorption, however, the syndiotactic and atactic stereoisomers are only partially retained. It means retention increases with molar mass and low molar mass iPP elutes without adsorption. Consequently tacticity can not be differentiated.

EGMBE was the first solvent which enabled the chromatographic separation of PE from iPP on silica gel [91,93]. The fractionation is based on the principle that iPP is

soluble at 140 °C, while PE with higher molar mass (> ~20 kg/mol) is insoluble [92]. Hence EGMBE acts as a good solvent and elutes iPP in SEC mode, while being non-solvent and precipitating PE on the stationary phase. The retained PE is later eluted in a gradient EGMBE→TCB, as TCB is a good solvent for both iPP and PE. Figure 4.7 shows the elution of iPP on TA 95 from EGMBE.

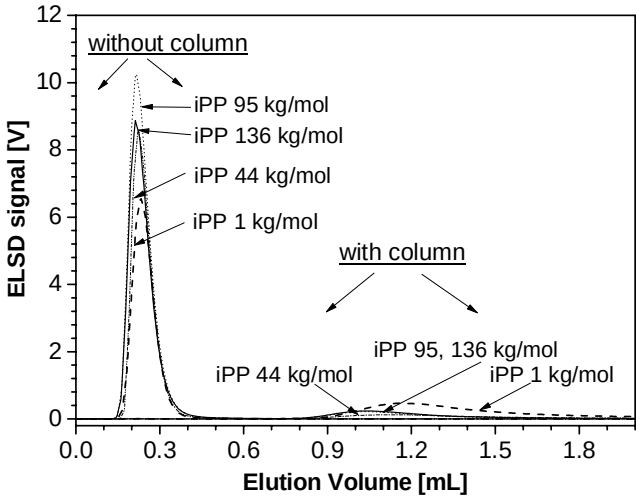
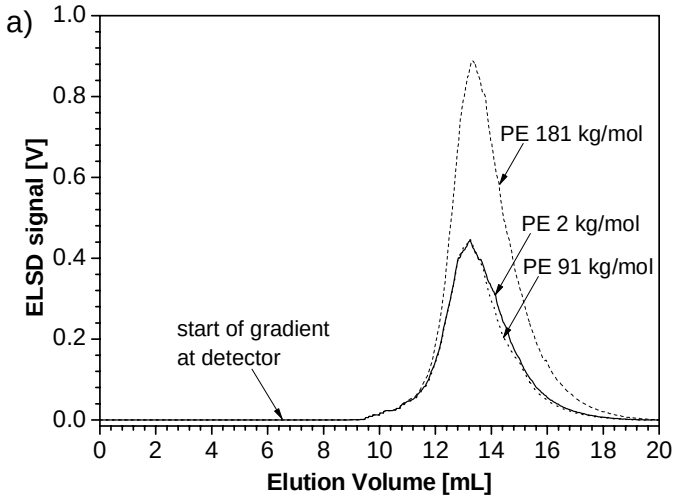
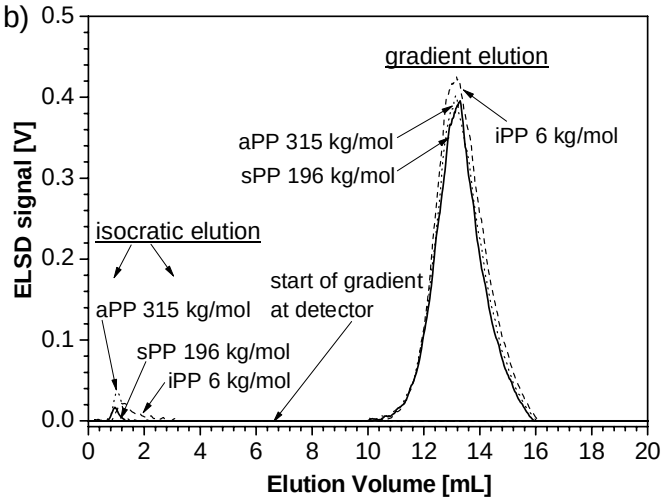


Figure 4.7: Overlay of chromatograms of iPP standards. Sorbent: TA 95. Mobile phase: EGMBE. Temperature: 160 °C. Chromatograph: PL XT- 220.

Pronounced adsorption of iPP can be observed from EGMBE onto TA 95. EGMBE is a polar solvent and could therefore enhance the adsorption of PP on carbonaceous sorbents. However, aPP and sPP with higher molar mass are not soluble in EGMBE and thus their elution behavior could not be tested.

It is known that the homologue with a higher molar mass is adsorbed preferentially on a carbon sorbent from a mixture of two n-alkanes (C8/C16, C8/C14, C6/C8 or C6/C14) [96,195]. Taking this into account, the retention behavior of PE and PP from n-decane was tested (Figure 4.8a, b and c).


a)
ELSD signal [V]
Elution Volume [mL]
PE 181 kg/mol
PE 2 kg/mol
PE 91 kg/mol
start of gradient
at detector


b)
ELSD signal [V]
Elution Volume [mL]
gradient elution
aPP 315 kg/mol
sPP 196 kg/mol
iPP 6 kg/mol
isocratic elution
aPP 315 kg/mol
sPP 196 kg/mol
iPP 6 kg/mol
start of gradient
at detector

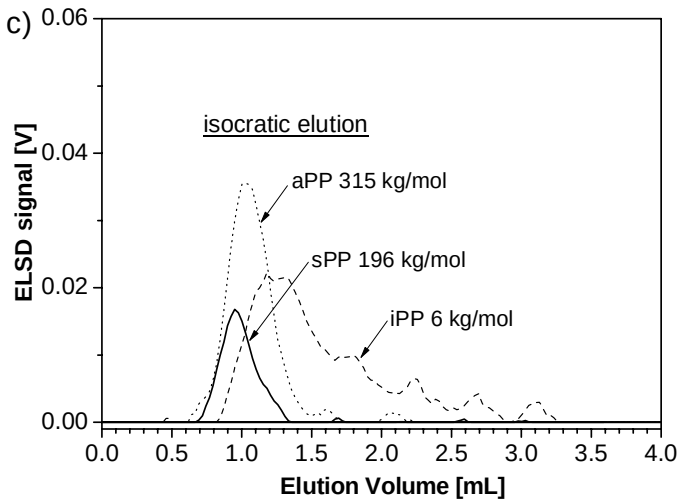


Figure 4.8: Overlay of chromatograms of a) fully retained PE standards and b) and c) almost fully retained PP standards. Sorbent: TA 95. Mobile phase: n-decane and gradient n-decane→TCB; Temperature: 140 °C.

PE standards are fully retained and elute only in the gradient n-decane→TCB, while PP standards are almost fully retained i.e., low molar mass is not retained, on TA 95 (Figure 4.8b and c). The enlarged scale in the isocratic elution range of PP (Figure 4.8c) illustrates that these polymer fractions elute in SEC mode. n-decane is the first non-polar solvent from which PE and PP were adsorbed on a sorbent as well as desorbed (Table 4.2).

4.1.3.3 Elution behavior on Hypercarb

Figure 4.9 shows the elution of PP on Hypercarb from n-decane.

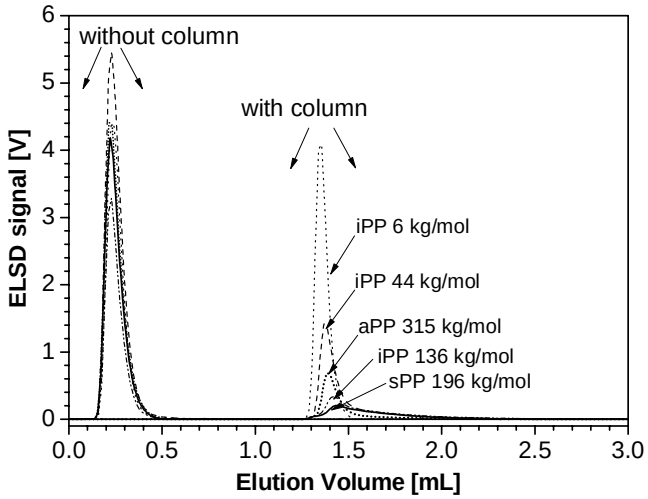
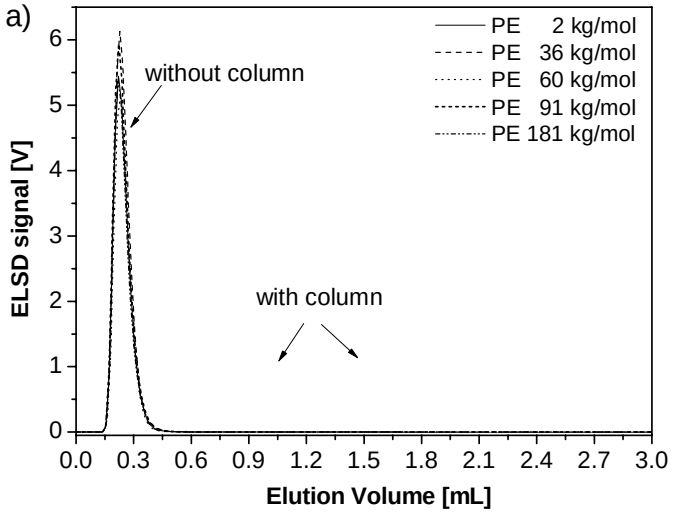
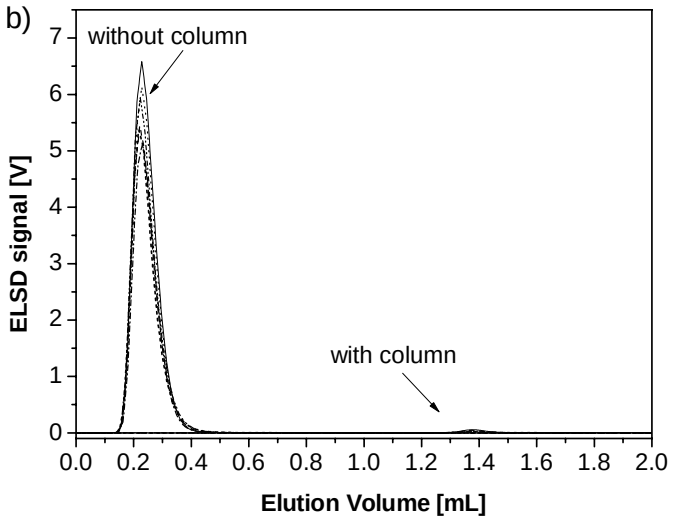


Figure 4.9: Overlay of chromatograms illustrating partial retention of PP standards. Sorbent: Hypercarb. Mobile phase: n-decane. Temperature: 140 °C. Chromatograph: PL XT- 220.

The peak areas eluted from the column are smaller than those obtained with capillary (i.e. without column), proving retention of PP. Moreover, the peak area obtained with column decreases with increasing molar mass of the polymer, indicating that the retention increases with the molar mass like previously observed for TA 95/n-decane.

Figure 4.10 illustrates the isocratic elution of PE and PP on Hypercarb from 2-ethyl-1-hexanol.


a)
PE 2 kg/mol
PE 36 kg/mol
PE 60 kg/mol
PE 91 kg/mol
PE 181 kg/mol
without column
with column
ELSD signal [V]
Elution Volume [mL]
0
1
2
3
4
5
6
0.0
0.3
0.6
0.9
1.2
1.5
1.8
2.1
2.4
2.7
3.0


b)
without column
with column
ELSD signal [V]
Elution Volume [mL]
0
1
2
3
4
5
6
7
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

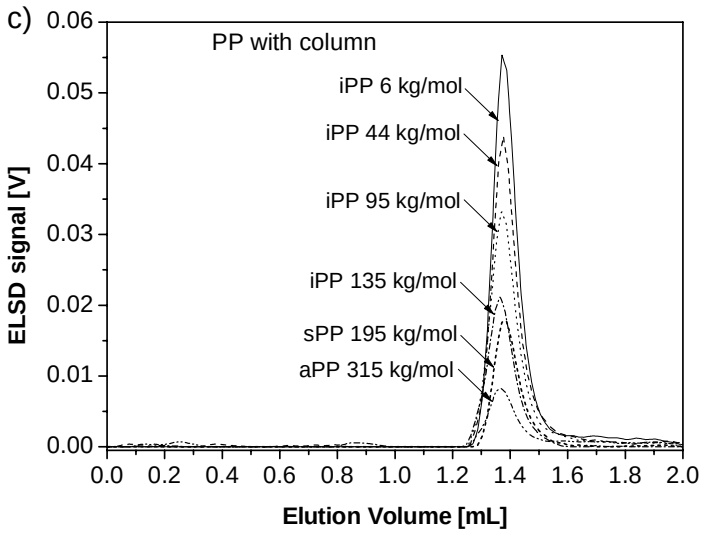


Figure 4.10: Overlay of chromatograms illustrating a) full retention of PE b) and c) almost full retention of PP standards. Sorbent: Hypercarb. Mobile phase: 2-ethyl-1-hexanol. Temperature: 160 °C. Chromatograph: PL XT- 220.

While PE is completely retained, low molar mass PP elutes without adsorption on Hypercarb. The peak area obtained with column is very small compared to that obtained without column for respective molar masses (Figure 4.10b and enlarged scale of PP eluted from column in Figure 4.10c). In contrast to the elution of PP in Hypercarb/1-decanol, Hypercarb/2-ethyl-1-hexanol does not discriminate with regard to tacticity.

As PE is completely retained, the separation of ethylene/1-hexene copolymers is tested in this chromatographic system (Figure 4.11). The retained polymers are eluted in the solvent gradient 2-ethyl-1-hexanol→TCB.

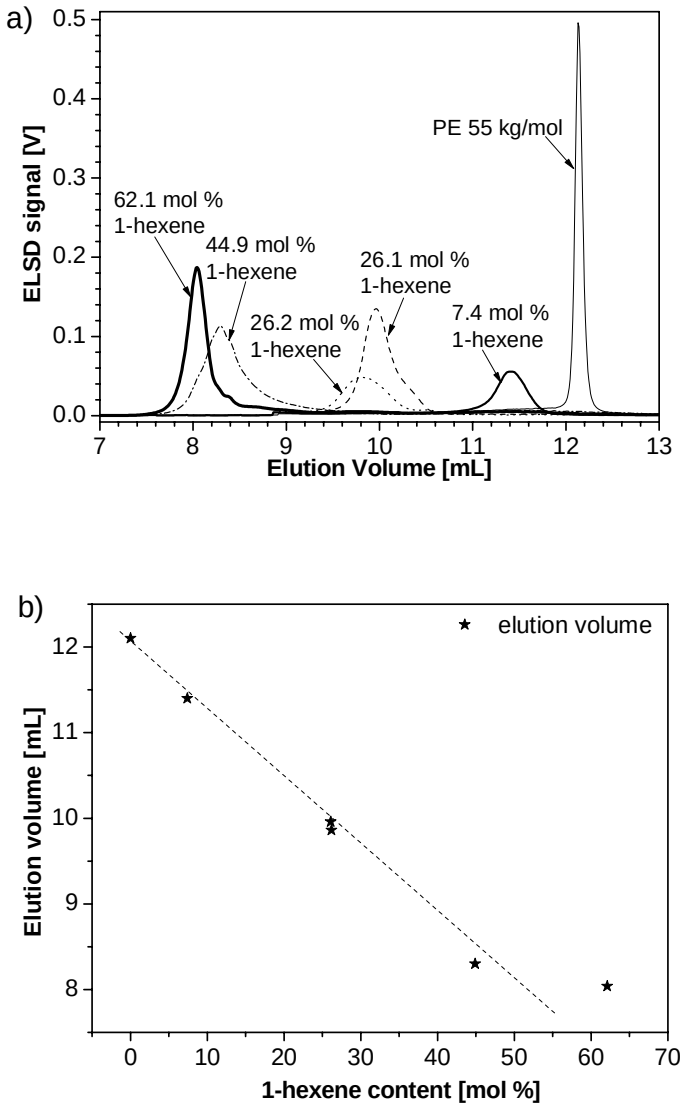


Figure 4.11: a) Overlay of chromatograms of random ethylene/1-hexene copolymers and b) correlation between the elution volume and the comonomer content. Sorbent: Hypercarb. Mobile phase: 2-ethyl-1-hexanol and gradient 2-ethyl-1-hexanol→TCB. Temperature: 160 °C. Chromatograph: PL XT-220.

Figure 4.11 demonstrates that ethylene/1-hexene copolymers can be separated with regard to their comonomer content in this chromatographic system. The elution volume at peak maximum decreases with increasing average content of 1-hexene (Figure 4.11b) as observed with ZirChrom-CARB/2-ethyl-1-hexanol→TCB. However, the latter chromatographic system fails to separate copolymers with a high content of 1-hexene (samples containing above 46 mol % of 1-hexene were not retained, Figure

4.4). The decrease in the elution volume can be attributed to the short chain branches resulting from the incorporation of 1-hexene comonomer [210].

It is interesting to compare the elution behavior of ethylene/1-hexene copolymers in ZirChrom-CARB/2-ethyl-1-hexanol→TCB and Hypercarb/2-ethyl-1-hexanol→TCB. Figure 4.12 compares the change of elution volume with regard to the 1-hexene content in these two chromatographic systems.

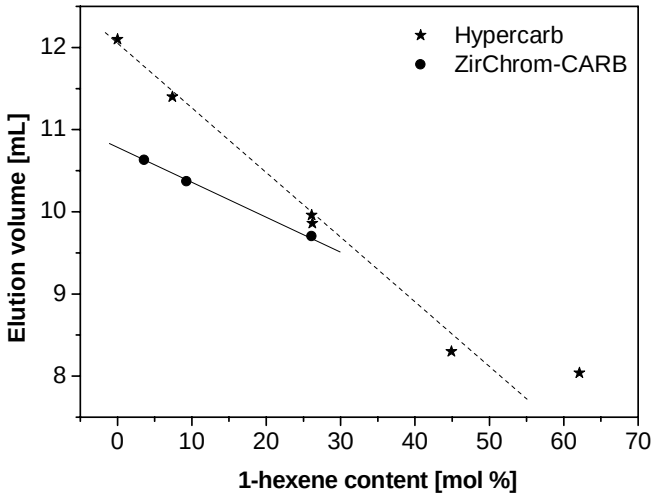


Figure 4.12: Comparison of the elution behavior of ethylene/1-hexene copolymers in Hypercarb/2-ethyl-1-hexanol→TCB and ZirChrom-CARB/2-ethyl-1-hexanol→TCB.

The elution volume linearily decreases with increasing comonomer content (i.e., with the incorporation of SCB to the polymer backbone) in these systems. However, the slope of the straight lines is different. While the elution volume drops more steeply and reaches a plateau at high comonomer content in Hypercarb/2-ethyl-1-hexanol→TCB, it drops moderately in ZirChrom-CARB/2-ethyl-1-hexanol→TCB, however, with no retention of copolymers having high 1-hexene content.

The elution behavior of PP and PE standards in all the tested sorbent-solvent systems is summarized in Table 4.2.

Table 4.2: Elution behavior of PE and PP standards with different carbon sorbent/solvent systems and the temperature of chromatographic system.

Sorbent	**ZirChrom-CARB**				**Hypercarb**				**TA 95**			
Polymer / **Solvent and temperature**	PE	iPP	aPP	sPP	PE	iPP	aPP	sPP	PE	iPP	aPP	sPP
2-ethyl-1-hexanol 160 °C	FR	E	E	E	FR	aFR	aFR	aFR	PR	PR	PR	PR
1-decanol 160 °C	aFR	E	E	E	FR	E	FR	FR	PR	E	PR	PR
hexylacetate 150 °C	FR	E	E	E	aFR	aFR	aFR	aFR	aFR	PR	PR	PR
cyclohexylacetate 160 °C	FR	E	E	E	FR	PR	PR	PR	PR	PR	PR	PR
cyclohexanone 140 °C	PR	E	E	E	PR	PR	PR	PR	FR	PR	PR	PR
n-decane 140 °C	PR	E	E	E	FR	PR	PR	PR	FR	aFR	aFR	aFR
EGMBE 165 °C	NS	PR	NS	NS	NS	PR	NS	NS	NS	aFR	NS	NS

Symbols: FR- fully retained, aFR-almost FR, PR-partially retained, E-eluted, NS-not soluble, NS- not soluble.

From the table it can be seen that while Hypercarb retains both PE and PP from almost all the tested solvents, TA 95 retains mainly in the high molar mass range and ZirChrom-CARB retained PE only.

A lattice fit between the graphite basal plane and the macromolecules in their extended conformation causes strong attractive interactions of the chains with the graphite surface. We suppose that these conclusions may be applied also for PE chains adsorbed on the tested carbon sorbents, such as Hypercarb and ZirChrom-

CARB. As these sorbents contain ideally (atomic) flat structures of graphite. In the case of carbon TA 95, however, functional groups (-OH, =CO, -COOH) present in the sorbent [195] could influence the conformations of PE chains.

4.2 Screening of carbonaceous sorbents and solvents for HT-HPLC of polyolefins - II

4.2.1 Aim of the study

It was shown in the previous chapter that interactive liquid chromatography opens hitherto new perspectives for the molecular characterization of polyolefins [211]. In this chapter the range of solvents will be expanded with particular focus on aromatic solvents and alcohols. The adsorption behavior of PE and PP on two new sorbents activated carbon (TA 120) and exfoliated graphite along with Hypercarb and ZirChrom-CARB from these solvents was studied. The activated carbon TA 120 used in this work has higher surface area (1960 m^2/g, see Chapter 5) than TA 95 which was used previously.

Particular attention was paid to the influence of molar mass on the elution of polymer and the capability to discriminate the stereoisomers in the case of PP, because these are important criteria for applying such sorbents in HPLC. To better understand the influence of solvent, molar mass and microstructure on the adsorption of polymer molecules quantitative information about the adsorption of the polymer on to a sorbent was obtained, by comparing the detector signal obtained with column with that obtained using a capillary instead.

In addition to that the retention of both PE and PP on Hypercarb and TA 120 from 1,2-dichloro- (ODCB) and 1,2,4-trichlorobenzene (TCB) at different temperatures (100 -160 °C) was also studied. The knowledge of which can be used to optimize the chromatographic separation. Thus this work elaborates one of the most interesting and innovative aspects of carbonaceous sorbents for liquid chromatography.

4.2.2 Solubility of PE and PP standards

The cloud point temperatures of PE and PP were measured in the respective solvent to find suitable temperature for chromatography and to classify the solvents with

regard to their salvation quality. Detailed description of the cloud point measurement can be found in the experimental section (Chapter 5). Solubility of PE or PP at the concentration of 1 mg/mL at the chromatographic temperature is given for solvents in which cloud point data couldnot be collected. The obtained solubility data is shown in Table 4.3a and b.

Table 4.3a: Solubility of PE (M_w - 260 kg/mol) at 1 mg/mL concentration.

Polymer / **Solvent**	**Cloud point temperature or solubility at chromatographic temperature [°C]**
Tetralin	87
Decalin	87
Mesitylene	84
p-Xylene	83
Xylene	84.5
1-hexanol	Not soluble at 150
1-heptanol	Not soluble at 160
1-octanol	Not soluble at 160
2-octanol	144
Isononanol	Not soluble at 160

Table 4.3b: Solubility of iPP (M_w **-** 136 kg/mol), aPP (M_w **-** 315 kg/mol) and sPP (M_w **-** 196 kg/mol) at 1 mg/mL.

Polymer / Solvent	Cloud point temperature or solubility at chromatographic temperature [°C]		
	iPP	**aPP**	**sPP**
Tetralin	70	Soluble at 140	Soluble at 140
Decalin	74	Soluble at 140	Soluble at 140
Mesitylene	140	Soluble at 140	Soluble at 140
p-Xylene	97.5	Soluble at 130	Soluble at 130
Xylene	62	Soluble at 130	Soluble at 130
1-hexanol	Not soluble at 150	Not soluble at 150	Not soluble at 150
1-heptanol	160	Soluble at 160	Soluble at 160
1-octanol	107	Soluble at 160	Soluble at 160
2-octanol	96	Soluble at 160	Soluble at 160
Isononanol	105	Soluble at 160	Soluble at 160

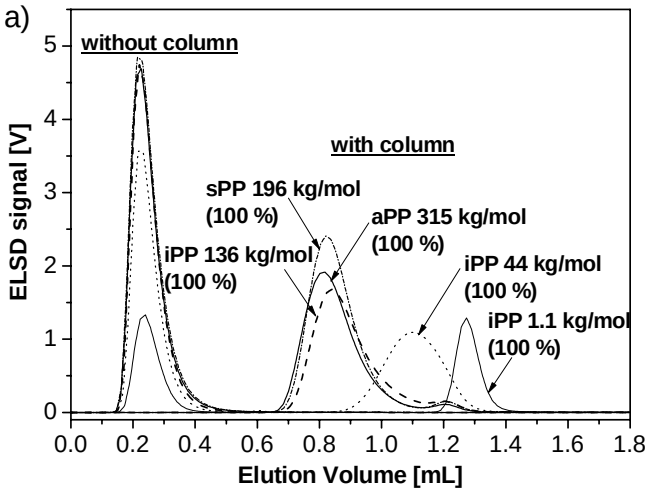
While both PE and PP are soluble in aromatic solvents at low temperatures (except iPP in mesitylene), alcohols require high temperatures to dissolve them. The solubility of PE and PP in alcohols decreases with decreasing carbon chain length, i.e. increasing polarity, of the alcohol. While 1-hexanol is a non-solvent to both PE and PP, only PP is soluble in other tested alcohols. Interestingly 2-octanol dissolves PE and PP at 160 °C which can be attributed to its relative less polarity.

4.2.3 Retention of PE and PP on carbonaceous sorbents from aromatic hydrocarbons and cycloalkanes

The polymer samples were dissolved in the respective mobile phase at a concentration of 1-2 mg/mL and injected into the column. Time and dissolution temperature were varied with solvent from 100 °C to 160 °C and 60 minutes to 180 minutes. 50 µL of each sample solution were injected. The mobile phase was either a single solvent or a binary solvent gradient. After the sample injection an isocratic elution with sample solvent follows for 3 minutes before starting a 10 min linear

gradient to reach 100 % TCB in all the gradients runs. The peak areas of the polymers eluting from the columns (CPA) were compared with those obtained when replacing the column by a simple capillary (CA). This enables to evaluate the extent of adsorption of the polymer on the sorbent, i.e., if a polymer is unretained (CPA = CA), partially retained (CPA < CA) or fully retained (polymer sample does not elutes from the column) on the column packing.

Figure 4.13a and b show the isocratic elution of PP with different molar mass and microstructure and PE standards on Hypercarb from tetralin.



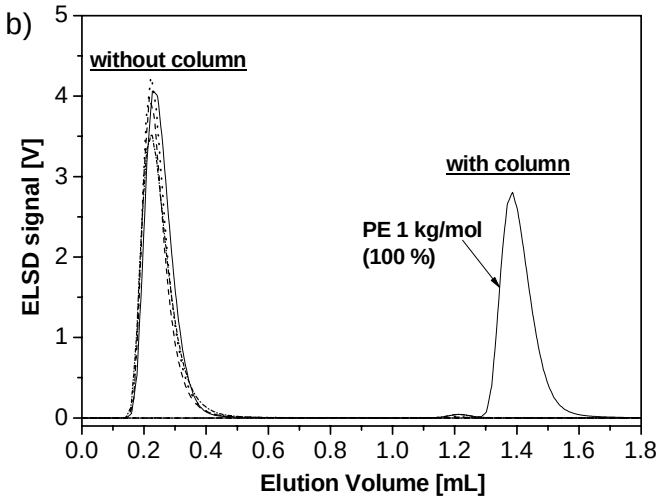


Figure 4.13: Overlay of the chromatograms: a) PP standards and b) PE standards; Sorbent: Hypercarb; Mobile phase: Tetralin; Temperature: 140 °C; Recovery given as CPA/CA below the molar mass. PE-standards with Mw ≥ 2 kg/mol are fully retained.

The recovery demonstrates that all stereoisomers of PP are not retained under these conditions (Figure 4.13a). Their elution volumes reflect differences in the molar mass, i.e. the lowest molar mass eluting last, implying that PP elutes in SEC mode. Unlike PP, PE is almost fully retained in this chromatographic system, except the lowest molar mass, 1 kg/mol (Figure 4.13b). Figure 4.14 shows representatively the elugrams of PE standards in decalin from Hypercarb and ZirChrom-CARB.

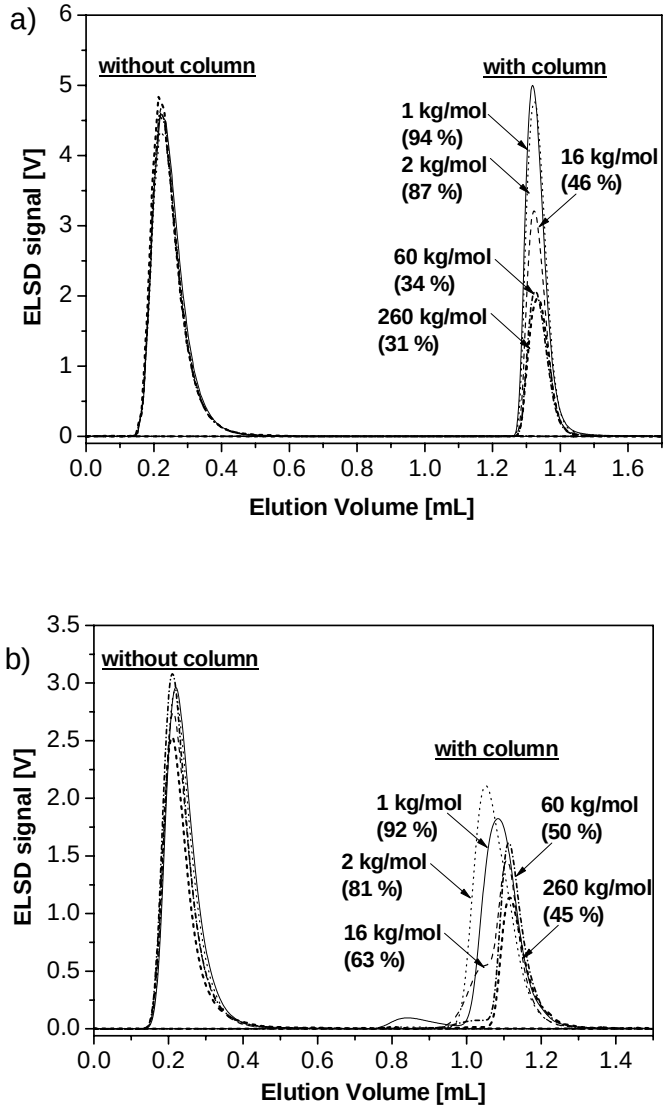


Figure 4.14: Overlay of chromatograms of PE standards eluted from a) Hypercarb and b) ZirChrom-CARB; Mobile phase: Decalin; Temperature: 140 °C; Percentage recovery calculated from CPA/CA is shown below the molar mass.

In both chromatographic systems the recovery decreases with the molar mass, i.e. the retention of the polymer increases with its molar mass. Due to insufficient attractive interactions between the analyte and the sorbent, the polymer is retained only to a certain extent. This type of elution where the recovery depends on the molar mass of the polymer is referred to as partial retention (PR). The recoveries show that PE is retained stronger on Hypercarb than on ZirChrom-CARB under the same

conditions. Additionally, the influence of the molar mass on the elution volume is more conspicuous in ZirChrom-CARB. The difference in the onset of the peaks for the respective molar mass in both systems is due to the dead volume of the column, i.e., the volume of the mobile phase that is present in the pores of the sorbent (pore volume) and in between the sorbent particles (interstitial volume).

Figure 4.15 illustrates the elution behavior of PP and PE standards on Hypercarb from mesitylene.

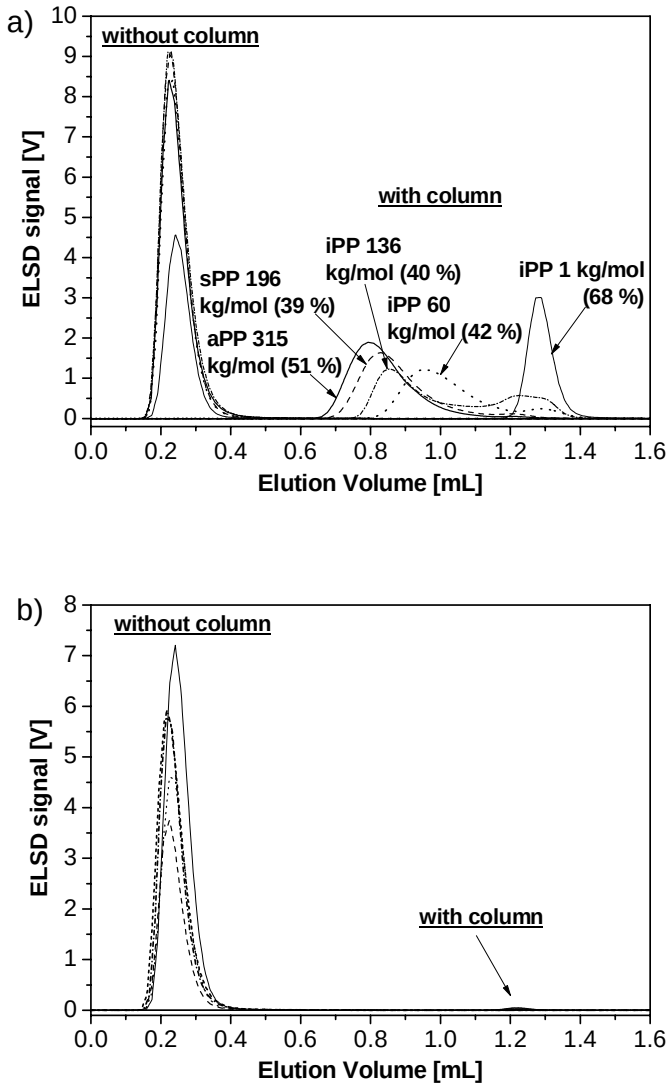


Figure 4.15: Overlay of chromatograms of a) PP standards and b) PE standards. Sorbent: Hypercarb; Mobile phase: Mesitylene; Temperature: 140 °C. Percentage recovery (CPA/CA) is indicated in the figure.

In the case of PP the chromatographic separation is mainly controlled by the molar mass and the polymers elute in SEC mode i.e., high molar mass polymers elute earlier than the low molar mass ones (Figure 4.15a). However, due to the narrow pore size distribution of the sorbent particles the molar mass separation is poor. iPP 60 and 136 kg/mol elute in more than one peak. As the elution volume is mainly influenced by the molar mass it may be assumed that low and high molar mass fractions present in these samples as a result of their higher dispersity (see experimental section, Chapter 5), elute at different elution volumes. The recovery indicates that a portion of the polymer is adsorbed and this increases with the molar mass. It can be speculated that the SEC separation is associated with secondary adsorption as it was found for some chromatographic systems [212]. Contrary to the elution of PP, PE samples are fully retained (FR) on Hypercarb from mesitylene (Figure 4.15b).

It is a common strategy in liquid chromatography to use solvent gradients as mobile phase, starting with an adsorption promoting solvent and ending with a desorption promoting one. The isocratic chromatographic system Hypercarb/tetralin (Figure 4.13) shows full adsorption of PE and elution of PP. However, when using a gradient tetralin→TCB the elution volume of PE becomes substantially dependent on its molar mass (Figure 4.16).

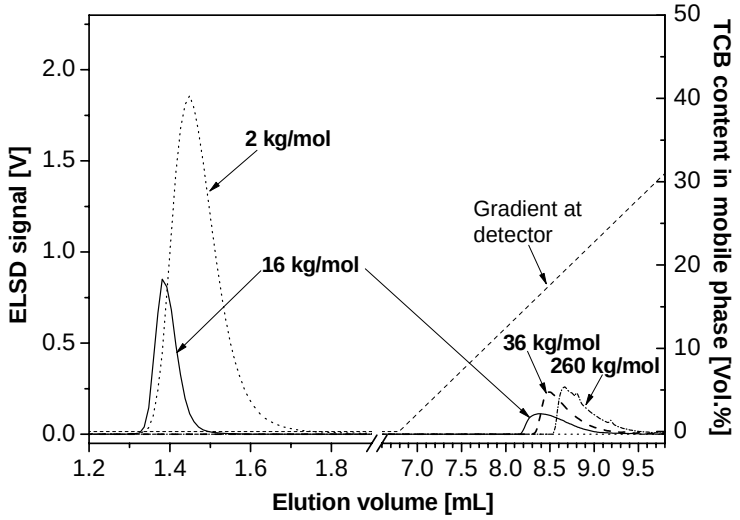


Figure 4.16: Overlay of the chromatograms of PE standards. Sorbent: Hypercarb; Mobile phase: gradient tetralin→TCB; Sample solvent: Tetralin; Temperature: 140 °C.

Samples of high molar mass elute in the gradient, while those of low molar mass as well as fractions of low molar mass, which are present in the high molar mass samples due to their higher dispersity, elute before, i.e. without being adsorbed. This molar mass dependence may be the result of a kinetic effect and can complicate the interpretation of data for unknown samples. Table 4.4 summarizes the elution behavior of PE and PP standards in the sorbent/solvent systems discussed. Additionally the elution behavior from TA 120 and exfoliated graphite is summarized.

Table 4.4: Overview of elution behavior of PE and PP standards in tested carbon sorbent/solvent systems.

a)

Sorbent	**Hypercarb**				**ZirChrom-Carb**			
Polymer / Solvent and temperature	iPP	aPP	sPP	PE	iPP	aPP	sPP	PE
Tetralin, 140 °C	E	E	E	aFR	E	E	E	E
Decalin, 140 °C	E	E	E	PR	E	E	E	PR
Mesitylene, 140 °C	PR	PR	PR	FR	E	E	E	E
p-Xylene, 130 °C	E	E	aFR	PR	E	E	E	E
Xylene, 130 °C	E	E	PR	aFR	E	E	E	E

b)

Sorbent	**TA 120**				**Exfoliated graphite**			
Polymer / Solvent and temperature	iPP	aPP	sPP	PE	iPP	aPP	sPP	PE
Tetralin, 140 °C	PR	PR	PR	PR	PR	PR	PR	aFR
Decalin, 140 °C	PR	PR	PR	aFR	PR	PR	PR	PR
Mesitylene, 140 °C	PR	PR	PR	FR	PR	PR	PR	aFR
p-Xylene, 130 °C	E	E	E	PR	PR	PR	PR	aFR
Xylene, 130 °C	PR	PR	PR	aFR	PR	PR	PR	aFR

Symbols: FR- fully retained (all PE or PP standards are fully retained on the column), aFR-almost FR (only PE or PP standard with M_w = ~1 kg/mol not retained); PR-partially retained (several PE or PP standards with M_w > 1 kg/mol not fully retained); E-not retained, i.e. polymer eluted from the column without adsorption.

The data shows that the elution behavior of PE and PP not only depends on the nature of a solvent but also on the nature of a column packing. In fact, all tested

sorbents contain carbon, however, with some differences in their chemical composition, surface area and structure: Hypercarb contains pure porous graphite [136]; TA 120 contains activated carbon with functionalized polar groups such as -OH, >C=O, -COOH originating from its synthesis; ZirChrom-CARB contains particles of zirconium oxide covered with a layer of carbon by vapour deposition [151] and exfoliated graphite is composed of graphite having an extraordinary large surface area [196]. As a consequence, Hypercarb has the largest and ZirChrom-CARB the lowest affinity to PE and PP within the solvents tested (Table 4.4) among the tested carbon-based sorbents. The expanded graphite and TA 120 show a similar extent of retention for PE and PP.

Liquid chromatographic separations of small molecules using Hypercarb and ZirChrom-CARB have been demonstrated in the literature. In these it was shown that ZirChrom-CARB behaves similar to Hypercarb with regard to the chromatographic separation of isomers [177]. However the picture is different for PE and PP, where both are not retained from most of the solvents tested on ZirChrom-CARB, while they are retained to a different extent on Hypercarb in our study. As the surface of both column packings consists of carbon a possible reason for this difference may be found in the microstructure of the materials: Hypercarb contains highly ordered and hexagonally arranged carbon atoms where the aromatic system of the graphite can interact with non-polar analytes due to dispersive interactions and as a result of the highly ordered surface can be structure selective for particular features of an analyte. On the contrary, carbon is present as a layer covering zirconia in ZirChrom-CARB, thereby replicating the original zirconia surface. The presence of any exposed sites of zirconia (carbon uncovered) may alter the chromatographic efficiency compared to pure carbon as exposed zirconia may interact with the solvent and analytes [183]. Additionally, a different surface structure may play a role.

Comparing the elution behavior from various solvents used in our present work PE is retained stronger from the methyl substituted benzenes than from tetralin and decalin. One will assume that the weaker interactions of the less planar aromatic and cycloaliphatic solvents, namely tetralin and decalin, with Hypercarb would enhance the retention of PE. Contradictory to that PE is retained stronger from the methyl benzenes than from tetralin or decalin, and within these the strongest retention is

found when mesitylene is used. Knox et al. showed that Hypercarb can separate isomers of xylene and other methyl benzenes and that mesitylene has the strongest affinity to Hypercarb, where methanol/water was used as mobile phase [136]. However, in order to rationalize the influence of the used solvents on the elution it has to be kept in mind that the interaction between the analyte and the stationary phase is a function of the analyte's solubility, hydrodynamic volume of the polymer coil as well as the interaction between the mobile and stationary phase.

4.2.4 Retention of PE and PP in carbon sorbent/alcohol→TCB systems

It was already shown that polyolefins can be separated on Hypercarb and ZirChrom-CARB from alcohols like 1-decanol and 2-ethyl-1-hexanol [211]. One of the most interesting features of the chromatographic system Hypercarb/1-decanol→TCB is its capability to resolve the stereoisomers of PP, while all of them elute without adsorption in ZirChrom-CARB/1-decanol→TCB. This creates the need to systematically investigate the influence of alcohols on the elution behavior of PE and PP on Hypercarb. For this purpose various alcohols, 1-hexanol, 1-heptanol, 1- and 2-octanol and isononanol, were selected. However, while both PE and PP are soluble in 2-octanol, they are not soluble in 1-hexanol. As only PP is soluble in the other alcohols considered here, the chromatographic elution of PP was studied for all cases and the data for PE is limited to 2-octanol (Table 4.5 and 4.6). Figure 4.17 shows the elution of PP standards with various molar mass and microstructure from Hypercarb using a gradient 2-octanol→TCB.

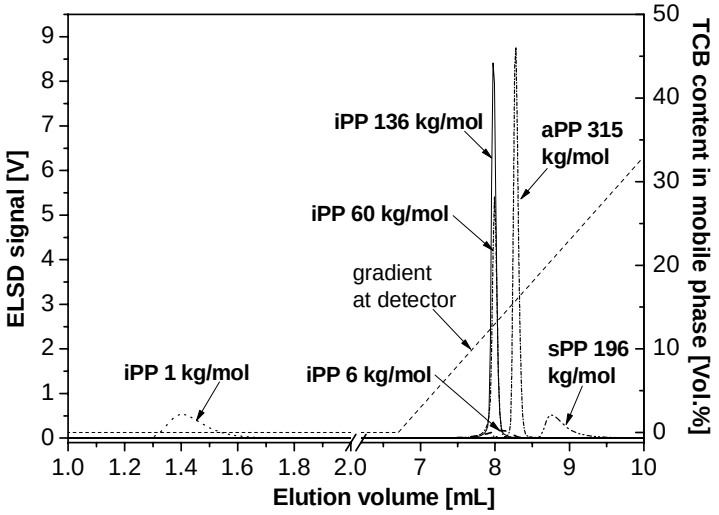


Figure 4.17: Overlay of chromatograms of PP standards. Sorbent: Hypercarb; Mobile phase: 2-octanol→TCB; Sample solvent: 2-octanol; Temperature: 160 °C.

All samples, except the lowest molar mass one (iPP 1 kg/mol), elute in the gradient. This system is able to discriminate isotactic, syndiotactic and atactic PP, with the elution order being iPP→aPP→sPP. While iPP elutes without adsorption in Hypercarb/1-decanol→TCB [99,104], it is pronouncedly adsorbed (except iPP 1 kg/mol) and eluted with the gradient in Hypercarb/2-octanol→TCB (Figure 4.17). Table 4.5 summarizes the retention of the stereoisomers of PP (calculated from the beginning of the gradient) on Hypercarb using a solvent gradient alcohol→TCB.

Table 4.5: Elution volumes at peak maximum (calculated from the beginning of the gradient) of stereoisomers of PP in Hypercarb/alcohol→TCB at 160 °C.

	Elution volume at peak maximum [mL]		
Polymer / **Solvent and temperature**	iPP (136 kg/mol)	aPP (315 kg/mol)	sPP (196 kg/mol)
1-heptanol, 160 °C	1.50	1.72	2.24
2-octanol, 160 °C	1.28	1.57	2.06
1-octanol, 160 °C	1.24	1.54	1.98
Isononanol, 160 °C	1.09	1.45	1.93

The retention of all stereoisomers decreases when the chain length of the alcohol is increased, with iPP being most affected. This is due to the fact that the interaction between non-polar polyolefins and the alcohol decreases with increasing polarity (or decreasing chain length) of the alcohol, thus it promotes the adsorption of polymer onto carbon sorbent. Within the tested octanols the isomeric (less polar) alcohol leads to slightly higher retention of all PP stereoisomers. Possible reasons are differences in the solvation of the polymer by the alcohol as well as the effect of the alcohol on the hydrodynamic volume of the macromolecules which maybe different for the three stereoisomers and less competition between polymer and alcohol to interact with the stationary phase. However, as data for these parameters are not available and thus an explanation for this cannot be given at this stage. Figure 4.18 illustrates the retention behavior of PE standards on Hypercarb using a solvent gradient 2-octanol→TCB.

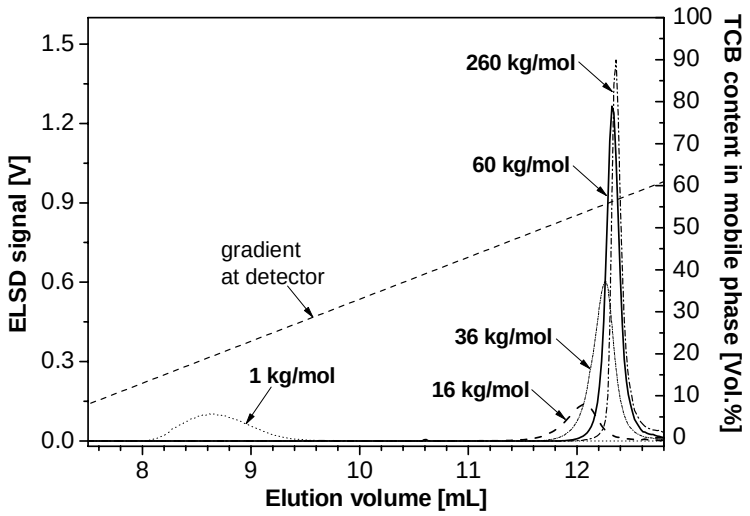
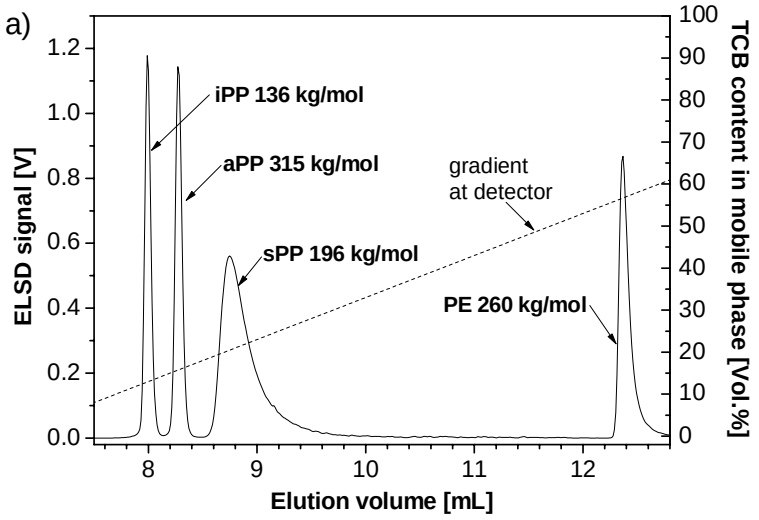


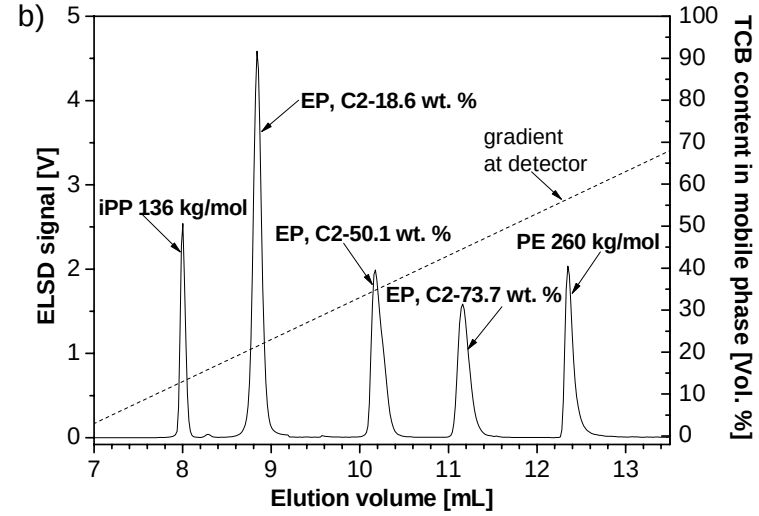
Figure 4.18: Overlay of the chromatograms of PE standards. Sorbent: Hypercarb; Mobile phase: gradient 2-octanol→TCB; Sample solvent: 2-octanol; Temperature: 160 °C.

All PE samples are fully retained on the sorbent and elute solely in the gradient. The molar mass exerts a strong influence on the retention of PE in this sorbent/solvent system, particularly in the low molar mass region. The retention increases with molar mass and above a certain value (60 kg/mol) the polymer elutes at constant elution

volume. Due to the insolubility of PE in the other alcohols (Table 4.3b) it was not possible to study the elution behavior of PE in these.

To evaluate if co-elution takes place under the conditions of Figure 4.18, a blend of all stereoisomeric forms of PP and PE was prepared and separated (Figure 4.19a). The elugrams of a blend of EP copolymers obtained using the same chromatographic system and the correlation between the elution volume at peak maximum and the ethylene content is illustrated in Figure 4.19b and 7c, respectively.





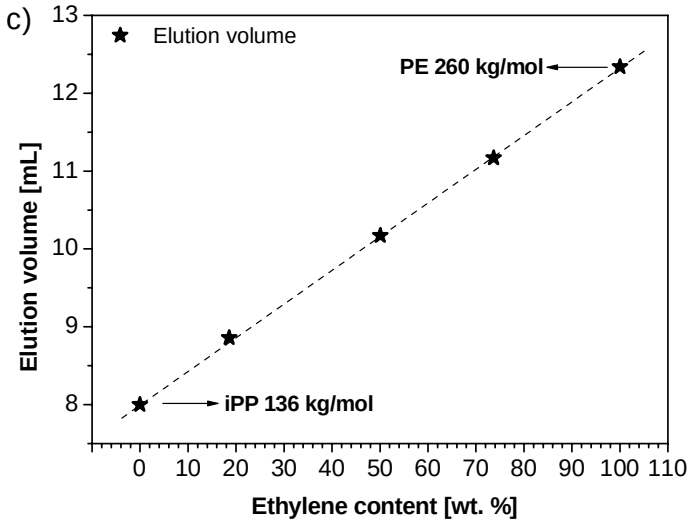


Figure 4.19: Overlay of the chromatograms: a) Blend of aPP, sPP, iPP and PE at weight ratio of 1:8:1:4, b) Blend of iPP, EP-copolymers and PE at weight ratio of 1:2:4 and c) elution volume at peak maximum as a function of average ethylene content. Sorbent: Hypercarb; Mobile phase: gradient 2-octanol→TCB; Sample solvent: 2-octanol; Temperature: 160 °C.

Hypercarb/2-octanol→TCB enables an excellent baseline separation of linear PE from PP as well as to resolve all stereoisomers of PP and no co-elution is observed (Figure 4.19a). EP copolymers are separated according to their ethylene content and fractionated from both corresponding homopolymers (Figure 4.19b). Correlating the ethylene content of the EP samples with the elution volume at peak maximum yields a straight line (Figure 4.19c). Extrapolating the fitted curve coincides with the elution volume of PE 260 kg/mol at 100 wt. % ethylene and iPP 136 kg/mol at 0 wt. % ethylene. This suggests that the PP units present in the EP samples are isotactic which could be expected from the catalyst used for synthesis [213]. Table 4.6 summarizes the extent of adsorption of the stereoforms of PP and PE on Hypercarb and ZirChrom-Carb in a semiquantitative way.

Table 4.6: Overview of the elution behaviour of PE and PP standards in carbon sorbent/alcohol→TCB.

Sorbent	**Hypercarb**				**ZirChrom-CARB**			
Polymer / **Solvent and temperature**	iPP	aPP	sPP	PE	iPP	aPP	sPP	PE
1-heptanol, 160 °C	aFR	FR	FR	NS	-	-	-	-
2-octanol, 160 °C	aFR	FR	FR	FR	E	E	PR	aFR
1-octanol, 160 °C	aFR	FR	FR	NS	-	-	-	-
Isononanol, 160 °C	aFR	FR	FR	NS	-	-	-	-

Symbols as in Table 4.4.

4.2.5 Retention of PE and PP on carbon-based stationary phases from TCB or ODCB

TCB has been used to desorb polyolefins from Hypercarb [54,99,101,129,214-216] and other carbonaceous sorbents [211,217] at 140 or 160 °C. It is known that temperature can alter the extent of adsorption of synthetic polymers on a solvent/sorbent interface [218]. Cong et al. [216] have applied a temperature gradient to separate ethylene/1-octene copolymers on Hypercarb using ODCB as mobile phase. It was demonstrated that depending on the temperature, ethylene/1-octene copolymers and PE are either fully retained in the column (at lower temperature) or eluted (at higher temperature). With the aim to study the influence of temperature on the retention of PE and PP, the elution of PE and PP standards from TCB and ODCB on Hypercarb and TA 120 at different temperatures was studied. The elugrams of PE 260 kg/mol from TCB on Hypercarb and TA 120 are shown in Figure 4.20a and b, respectively.

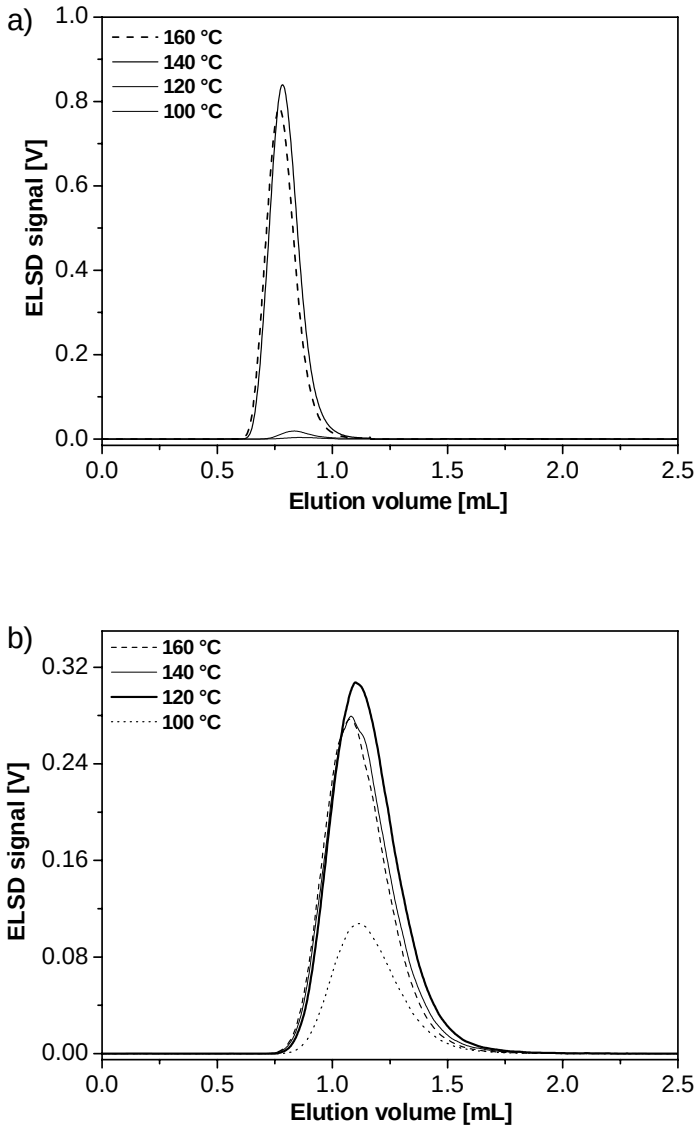


Figure 4.20: Overlay of chromatograms of PE 260 kg/mol eluted from a) Hypercarb and b) TA 120 at different temperatures; Mobile phase: TCB; Sample solvent: TCB at 160 °C.

While PE (260 kg/mol) is partially retained on TA 120 at 100 °C (Figure 4.20b), it is pronouncedly retained on Hypercarb at 100 and 120 °C (Figure 4.20a). On the contrary PP standards elute without any retention on both, Hypercarb and TA 120 within the tested temperature range (Table 4.7). As PE elutes without adsorption at 160 °C from both TCB and ODCB on these sorbents, the peak area obtained at 160 °C was used as reference to evaluate the extent of adsorption at other temperatures. The recovery in case of partial retention is then derived from the peak area ratios of

polymer eluted at 160 °C and that eluting at the respective temperature. Table 4.7 gives an overview of the retention behavior of PE and the stereoisomers of PP on Hypercarb and TA 120.

Table 4.7: Overview of the elution behavior of PE and PP standards in TCB and ODCB from carbon sorbents at different temperature.

Sorbent	**Hypercarb**				**TA 120**			
Mobile phase	TCB	ODCB	TCB	ODCB	TCB	ODCB	TCB	ODCB
Polymer / **Temperature [°C]**	PE*		iPP**, aPP, sPP		PE*		iPP**, aPP, sPP	
160	E	E	E	E	E	E	E	E
140	E	PR (72 %)	E	E	E	E	E	E
120	FR	FR	E	E	E	E	E	E
100	FR	FR	E	E	PR (44 %)	E	E	E

Symbols as in Table 4.4. *M_w = 260 kg/mol; **M_w = 136 kg/mol.

As PE and PP usually do not precipitate or crystallize above 100 °C from a dilute solution in ODCB or TCB the described data confirm that depending on the solvent used, PE can be adsorbed on a graphitic carbon sorbent at lower temperatures (100 - 120 °C) or desorbed at higher temperatures (140 - 160 °C). The difference in the retention behavior of PE with TCB and ODCB supports the observation of a lower anchoring temperature of PE in TCB than in ODCB on Hypercarb [216].

4.2.6 Elution behavior of ethylene/1-olefin copolymers in Hypercarb/alcohol→TCB

Polymer samples

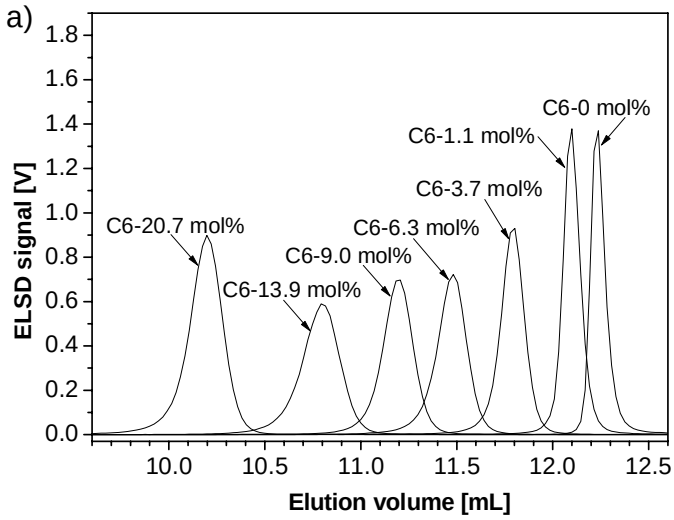
It was shown that the incorporation of 1-hexene decreases the adsorption of PE on carbon based sorbents (Hypercarb and ZirChrom-CARB). An interesting question is therefore how the chain length of the comonomer affects the decrease in adsorption, i.e. the reduction in elution volume. For this purpose, copolymers of ethylene and 1-olefins were prepared using single site catalysts. The average values of their

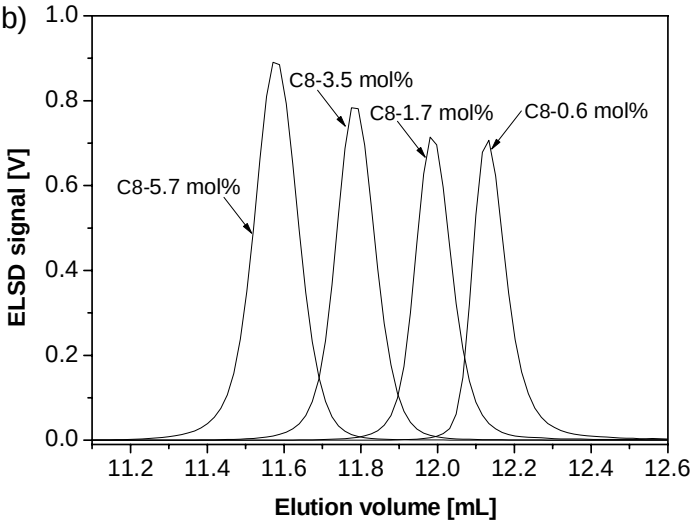
chemical composition determined by NMR and the average molar mass (using SEC) are summarized in Table 4.8.

Table 4.8: Weight average molar mass (M_w), dispersity (D) and average chemical composition of polymer samples.

Sample code	Comonomer content [mol%] (NMR)	Comonomer	M_w [kg/mol]	D
EH1	0	1-hexene (C6)	175	2.9
EH2	0.4		89	2.2
EH3	1.1		105	2.6
EH4	2.2		81	2.0
EH5	3.7		64	1.8
EH6	5.1		96	2.1
EH7	5.8		104	2.3
EH8	6.3		66	1.8
EH9	9.0		93	2.2
EH10	13.9		112	1.9
EH11	20.7		101	2.0
EO1	0.4	1-octene (C8)	73	2.0
EO2	0.6		118	3.5
EO3	1.7		90	2.9
EO4	3.5		92	2.3
EO5	5.7		127	2.7
EOD1	1.5	1-octadecene (C18)	103	2.1
EOD2	1.7		94	2.0
EOD3	3.3		119	1.9
EOD4	4.1		78	2.2
EOD5	4.7		86	2.0
EOD6	6.9		98	2.1

Figure 4.21 illustrates the elution behavior of ethylene/1-olefin copolymers in Hypercarb/2-octanol→TCB and the correlation between comonomer content and elution volume at peak maximum.


a)
ELSD signal [V]
Elution volume [mL]
C6-0 mol%
C6-1.1 mol%
C6-3.7 mol%
C6-6.3 mol%
C6-9.0 mol%
C6-13.9 mol%
C6-20.7 mol%


b)
ELSD signal [V]
Elution volume [mL]
C8-3.5 mol%
C8-1.7 mol%
C8-0.6 mol%
C8-5.7 mol%

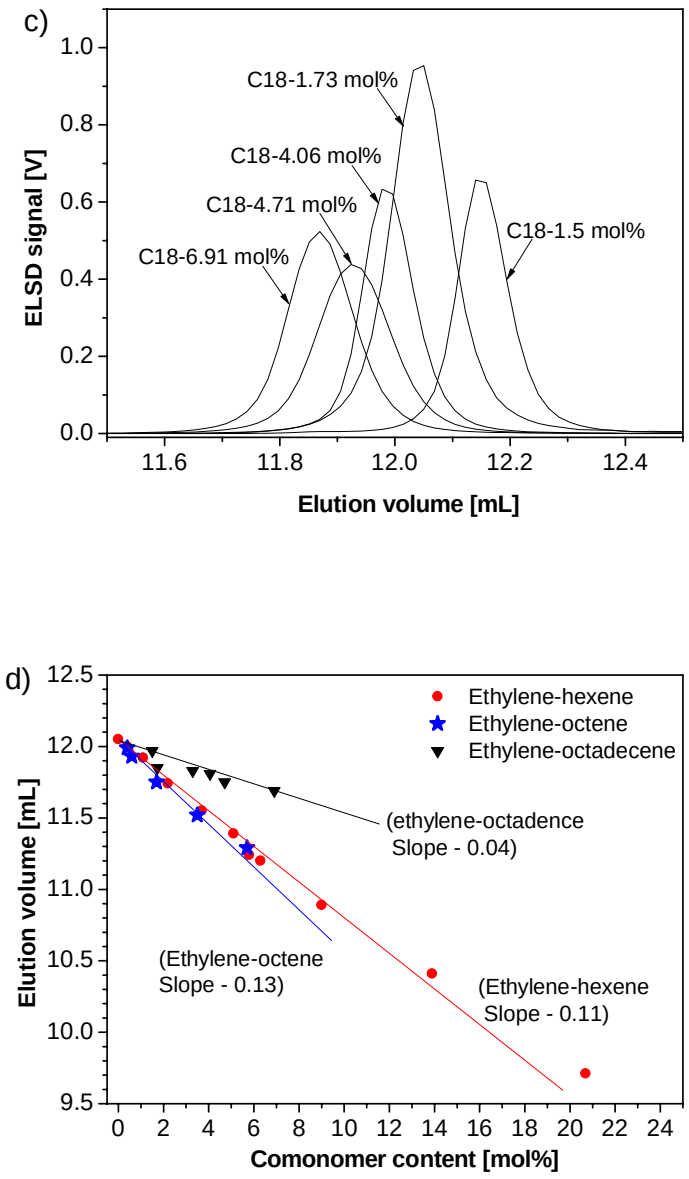


Figure 4.21: Overlay of chromatograms of a) ethylene/1-hexene, b) ethylene/1-octene and c) ethylene/1-octadecene copolymer samples and d) correlation between comonomer content and elution volume at peak maximum of all copolymer samples. Sorbent: Hypercarb; Mobile phase: gradient 2-octanol→TCB; Sample solvent: 2-octanol; Temperature: 160 °C.

All copolymer samples are separated according to their comonomer content. The elution volume at peak maximum decreases with increasing average comonomer content of the copolymer. It is assumed that the branches, i.e., side chains which are present due to the incorporation of comonomer, decrease the probability of

orientation of the macromolecules in a flat conformation on the graphite surface leading to decrease in van der Waals interactions between polymer backbone and Hypercarb [104]. Hence, the higher the content of side chain branches, the lesser the retention of the polymer. The width of the chromatogram can be taken as the CCD of the copolymer, as the retention is controlled mainly by the chemical composition of the samples. The CCD is broader in those copolymers with high comonomer content.

The correlation between comonomer content and elution volume at the peak maximum (Figure 4.21d) gives more insight into the elution behavior. It can be seen that the drop in elution volume increases with increasing length of the side chain. However in the case of ethylene/1-octadecene the decrease in elution volume is relatively less compared to other olefin copolymers with comparable comonomer content. It can be hypothesized that as the number of methylene units of the side increases the latter would also interact with the Hypercarb surface like the back bone. Owing to that the steric hindrance by the side chain for the flat alignment of polymer backbone on carbon surface is apparent only until a certain chain length. The same elution order is observed in Hypercarb/2-ethyl-1-hexanol→TCB and Hypercarb/1-decanol→TCB. Figure 4.22 illustrates the elution behavior of ethylene/1-octene copolymers in 1-decanol→TCB, 2-ethyl-1-hexanol→TCB and 2-octanol→TCB as Hypercarb as the stationary phase.

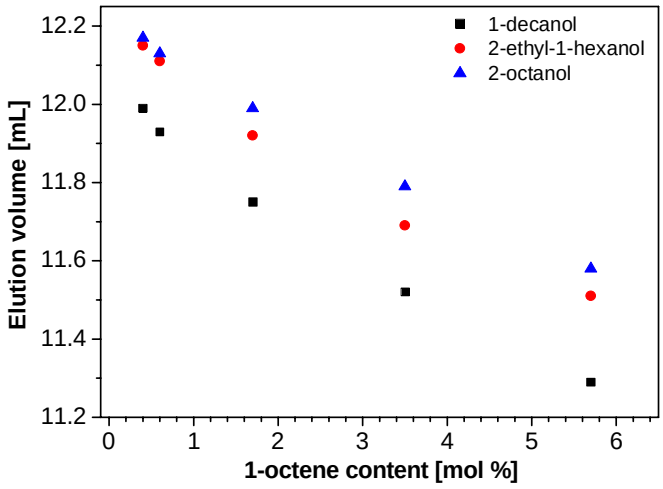


Figure 4.22: Elution behavior of ethylene/1-octene copolymers in 1-decanol/Hypercarb, 2-ethyl-1-hexanol/Hypercarb and 2-octanol→TCB/ Hypercarb. Sorbent: Hypercarb; Mobile phase: gradient alcohol→TCB; Sample solvent: respective alcohol in mobile phase; Temperature: 160 °C.

The elution volume decreases with increasing 1-octene content in all the chromatographic systems as observed before. However, the retention strengths of the copolymers differ with alcohol; strongest retention of copolymers is observed in 2-octanol. Even though, the copolymers with low or no 1-octene content are retained in 2-ethyl-1-hexanol as strong as in 2-octanol, the retention difference is seen in the high comonomer content range where the elution volume drops significantly in 2-ethyl-1-hexanol. The same elution behavior is observed in 1-decanol, which offers relatively the lowest retention of the copolymers. The strongest retention of copolymers in 2-octanol could be attributed to the high polarity of the solvent, which promotes strong retention on Hypercarb.

Table 4.9 summarizes the elution volumes of olefin copolymers in all tested chromatographic systems.

Table 4.9: Elution volumes at peak maximum of ethylene/1-olefin copolymers in Hypercarb/alcohol→TCB.

Sample code	Comonomer content [mol %] (NMR)	Comonomer	Elution volume [mL]		
			Mobile phase		
			1-decanol→TCB	2-EH→TCB	2-octanol→TCB
EH1	0	1-hexene (C6)	12.05	12.21	12.23
EH2	0.4		12.00	12.14	12.18
EH3	1.1		11.92	12.06	12.09
EH4	2.2		11.74	11.93	11.96
EH5	3.7		11.55	11.91	11.80
EH6	5.1		11.39	11.65	11.65
EH7	5.8		11.24	11.54	11.53
EH8	6.3		11.20	11.47	11.48
EH9	9.0		10.89	11.17	11.19
EH10	13.9		10.41	10.79	10.80
EH11	20.7		09.71	10.18	10.20
EO1	0.4	1-octene (C8)	11.99	12.15	12.17
EO2	0.6		11.93	12.11	12.13
EO3	1.7		11.75	11.92	11.99
EO4	3.5		11.52	11.69	11.79
EO5	5.7		11.29	11.51	11.58
EOD1	1.5	1-octadecene (C18)	11.97	12.1	12.15
EOD2	1.7		11.85	11.97	12.03
EOD3	3.3		11.83	11.99	12.02
EOD4	4.1		11.81	11.96	11.99
EOD5	4.7		11.75	11.89	11.93
EOD6	6.9		11.69	11.86	11.87

It illustrates that strongest retention of copolymers is from 2-octanol followed by 2-ethyl-1-hexanol and 1-decanol. These results support our assumption that the chain length of the alcohol or polarity of the solvent influences the retention of polymer on carbon surface.

4.3 Separation of EP Copolymers and EPDM terpolymers using HT-HPLC

4.3.1 Aim of the study

EPDM is generally amorphous and therefore does not crystallize from solution. As a consequence fractionation techniques based on crystallization like CRYSTAF or TREF can not be used to analyze their CCD. With aim to separate EPDM-terpolymers and EP-copolymers two different sorbent/solvent systems were chosen and tested with regard to their capability to separate these samples according to their chemical composition,

4.3.2 Polymer samples

To simplify the understanding of elution behavior and mechanism of separation, influence of individual parameters (ethylene, diene, molar mass and long chain branching) was studied. For this purpose four series of polymer samples were prepared in the laboratory of Lanxess Elastomers (DSM Elastomers), Geelen, The Netherlands:

1) EP copolymers varying in ethylene content;
2) EP copolymers having similar ethylene content but varying in molar mass;
3) EPDM varying in ENB content, while keeping the content of ethylene constant;
4) EPDM, which differ in MMD and long chain branching, but have very similar average chemical composition.

The samples of series 1 were made in a batch polymerization reactor using advanced single site catalysts. In order to ensure a narrow compositional and molar mass distribution the conversion was kept low and the gas composition above the liquid phase was kept constant by a constant flow and ratio of ethylene and propylene. The samples of series 2-4 were prepared in a continuous flow stirred tank reactor using an advanced single site catalyst. The well mixed behavior and constant polymerization conditions ensured a narrow CCD and MMD of the polymers.

Only when using VNB the MWD became broader due to branching reactions in the reactor.

The average contents of ethylene (C2), propylene (C3), ENB and VNB in weight percentage (wt.-%) were determined with NMR spectroscopy. Weight-average molar masses (M_w) of the copolymers and dispersity (D) determined by SEC are summarized in Table 4.10. The content of LCB of EPDM samples was characterized by melt rheology according to the procedure described by Booij [219] and expressed by the value Δδ.

Table 4.10: Average comonomer content, weight-average molar mass (M_w) and dispersity (D) of ethylene-propylene copolymers and ethylene-propylene-diene polymers.

Series 1: EP copolymers – variation in EP ratio.

Sample No.	**C2 [wt. %]**	**C3 [wt. %]**	**M_w [kg/mol]**	**D**
1	18.6	81.4	180	2.0
2	33.2	66.8	1405	2.1
3	42.5	57.5	2270	2.0
4	45.2	54.9	1160	1.9
5	48.2	51.8	405	3.2
6	50.1	49.9	2075	2.2
7	52.8	47.2	755	2.2
8	57.8	42.2	1530	2.1
9	60.5	39.5	290	2.2
10	63.4	36.6	1585	1.9
11	65.9	34.1	650	2.0
12	73.7	26.3	2075	1.9

Series 2: EP copolymers - Variation in average molar mass.

Sample No.	C2 [wt. %]	C3 [wt. %]	M_w [kg/mol]	D
13	42.5	57.5	580	2.1
14	42.6	57.4	490	2.1
15	42.8	57.2	715	2.1
16	42.9	57.1	310	2.1
17	43.8	56.2	250	2.1

Series 3: Ethylene-propylene-ENB terpolymers - Variation in content of ENB.

Sample No.	C2 [wt. %]	C3 [wt. %]	ENB [wt. %]	M_w [kg/mol]	D
18	49	43.8	7.2	540	2.3
19	49	47.2	3.8	515	2.1
20	51.3	45.8	2.9	530	2.2
21	51.8	48.2	0	520	2.4

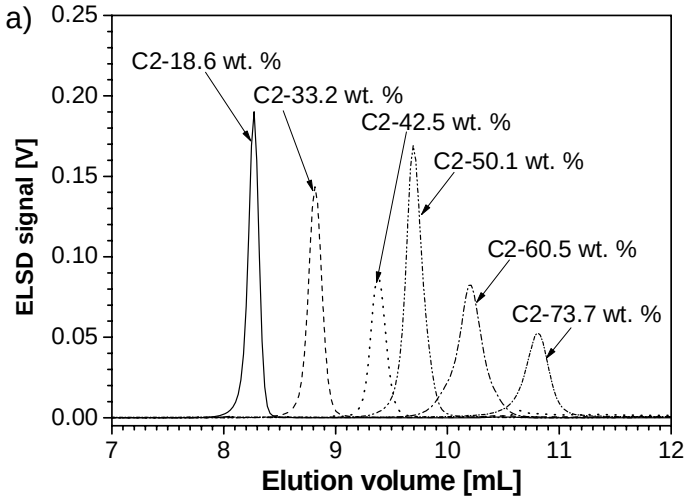
Series 4: Ethylene-propylene-ENB-VNB copolymers - Variation in LCB.

Sample No.	C2 [wt. %]	C3 [wt. %]	ENB [wt. %]	VNB [wt. %]	Branching Δδ	M_w [kg/mol]	D
22	52.6	44.3	0.4	2.7	23	425	3.1
23	55.2	41.6	0.4	2.8	12.7	660	3.6
24	55.4	41.1	0.7	2.8	8.8	645	4.1
25	55.6	40.9	0.6	2.9	5.5	550	3.7

4.3.3 Separation using Hypercarb/1-decanol→TCB

4.3.3.1 Influence of ethylene content on retention of EP

As a starting point the chromatographic system Hypercarb/1-decanol→TCB which separates semicrystalline copolymers of ethylene and propylene with 1-alkenes was chosen [104]. To have all the samples completely dissolved, a temperature of 160 °C was used in the HPLC experiments. The polymer samples were injected into the Hypercarb column and eluted in the gradient 1-decanol→TCB. The elugrams of the EP samples which vary in their ethylene content are shown in Figure 4.23a and the relationship between the elution volume at peak maximum and the ethylene content in Figure 4.23b.



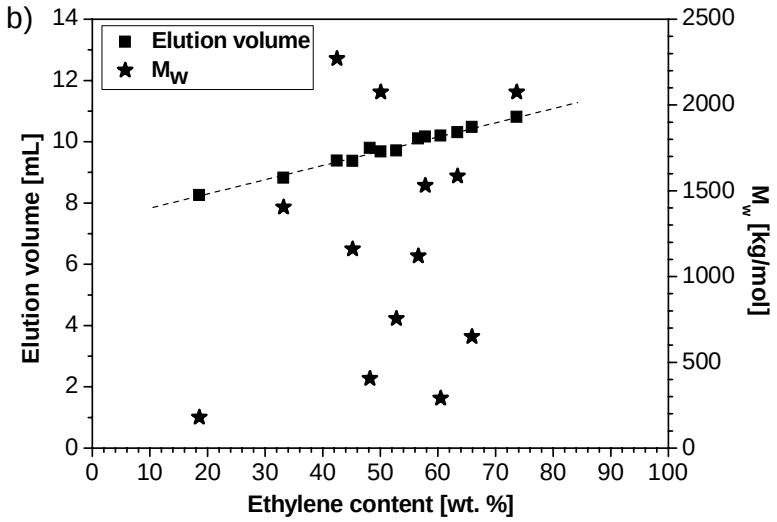


Figure 4.23: a) Overlay of chromatograms of EP copolymers and b) average chemical composition (content of ethylene) versus elution volume and weight-average molar mass of EP samples. Sorbent: Hypercarb; Mobile phase: gradient 1-decanol→TCB at a flow rate of 1 mL/minute; Temperature: 160 °C.

While sample No. 12, which has the highest ethylene content (73.7 wt. %), elutes at 41 vol. % of TCB in the gradient, the sample with the lowest ethylene content (sample No. 1, 18.6 wt. % ethylene) elutes already at 16 vol. % of TCB. The elution volume of the copolymer samples increases linearly with the ethylene content. On the other hand, values of the M_w are randomly scattered in Figure 4.23b, i.e., they do not correlate with the elution volume and suggest that the retention is not influenced by the molar mass. The chromatograms of the EP copolymers in Figure 4.23a have a peak width of ~ 0.5 mL, which corresponds to a compositional range of ~ 11 wt. % ethylene. It means that their CCD is relatively narrow and thus they are suitable to calibrate the elution volume axis.

Figure 4.24 illustrates the separation of a blend of EP copolymer in this chromatographic system.

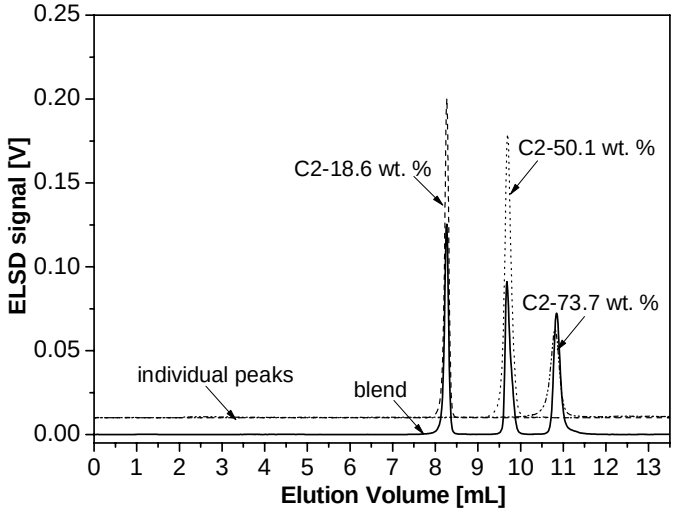


Figure 4.24: Overlay of chromatograms of individual injection peaks and blend of EP copolymers C2-18.6 wt. %, C2-50.1 wt. %, C2-73.7 wt. %. Sorbent: Hypercarb; Mobile phase: gradient 1-decanol→TCB at a flow rate of 1 mL/minute; Temperature: 160 °C.

All samples are well baseline separated even from the blend and elute exactly at the same elution volume obtained when injecting the copolymer individually. This emphasizes the selectivity of this chromatographic system towards ethylene sequences. The difference in the peaks areas (ELSD response) of the individually injected sample peaks and blend peaks is due to the variation in the injected sample concentration.

4.3.3.2 Influence of molar mass on retention of EP

Figure 4.23b demonstrates that the retention of the EP copolymers does not correlate with their average molar mass. To study the influence of the molar mass on the elution in detail samples of identical composition and differing in their molar mass were chosen. The overlay of the elugrams is shown in Figure 4.25.

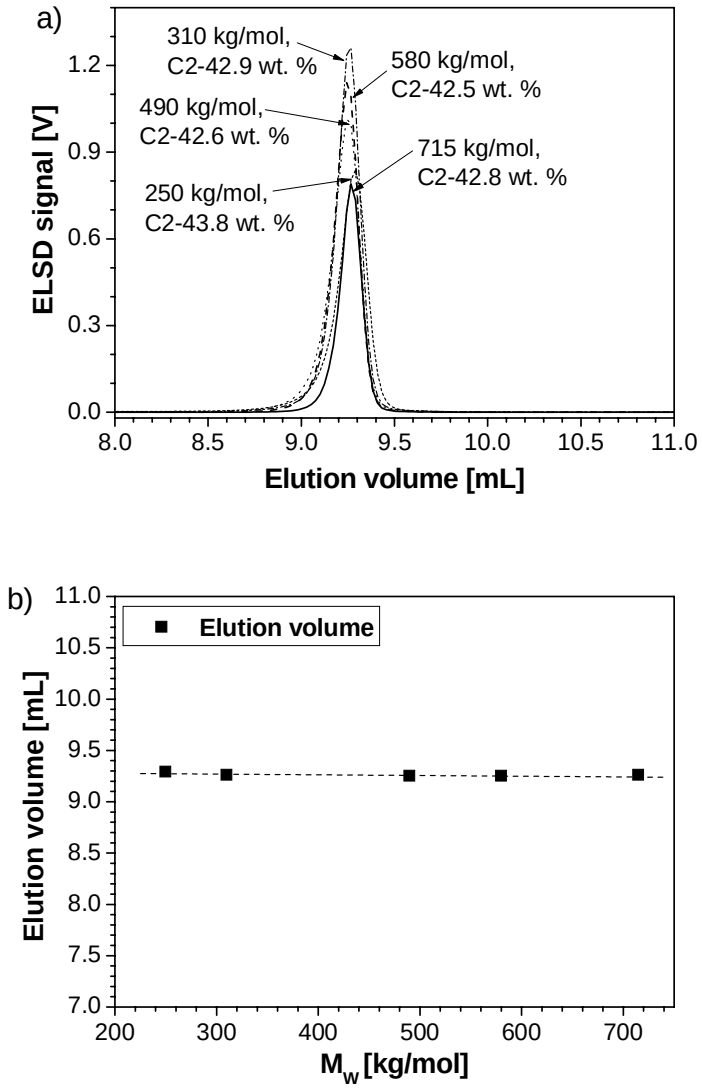


Figure 4.25: a) Overlay of the chromatograms of EP copolymer samples which vary in molar mass b) M_w versus elution volume of EP samples at the peak maximum. Experimental conditions as in Figure 4.23.

These data confirm our assumption from figure 4.23b that the molar mass does not influence the elution behavior within the range tested.

4.3.3.3 Influence of diene content on retention of EPDM

An interesting question is how the incorporation of diene influences the chromatographic retention. This is of crucial importance, because this gives insight

into the heterogeneity of the polymers with regard to their cross-link sites. This knowledge can be used to tailor these materials for particular applications. To evaluate how the incorporation of a diene influences the retention behavior samples with almost the same ethylene content (series 3) were selected and analyzed. These samples vary in their ENB content. As the ethylene content is very similar in these samples, which means that the adsorption of methylene units is kept constant, the influence of the presence of ENB units on the retention may be singled out. Figure 4.26a shows the overlay of the corresponding chromatograms.

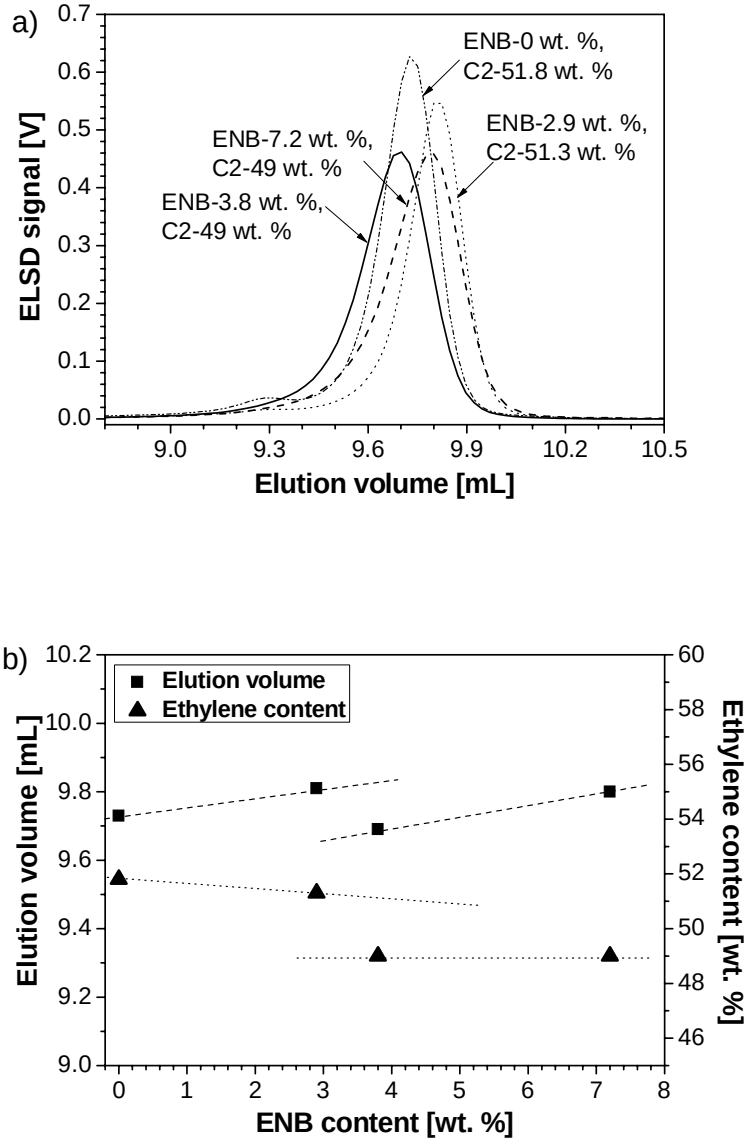


Figure 4.26: a) Overlay of chromatograms of EPDM samples which vary in their ENB content and b) ENB content plotted against elution volume and ethylene content. Experimental conditions as in Figure 4.23.

The comparison of the elution volumes at maximum of the samples with the same ethylene content 49 wt. % (sample No. 18 and 19) and 51.3 wt. % (sample No. 20 and 21) is shown in Figure 4.26b. It can be clearly observed that within these pairs the sample with higher ENB content elutes at higher elution volume. This demonstrates that, while the concentration of ethylene determines the elution volume in EP copolymers (Figure 4.23), the content of both ethylene and ENB influence the retention of EPDM (Figure 4.26). As a hypothesis we tentatively attribute this to the presence of the unsaturation left in the incorporated ENB which could promote adsorption via attractive interaction with the graphite. Similar observations have been made for unsaturated fatty acid esters [220]. To quantify the contribution of ENB alone on the chromatographic retention, a larger number of samples covering a wide range of ENB content will be needed.

4.3.3.4 Influence of long chain branching on retention of EPDM

To probe the influence of long chain branching on the elution behavior samples with different content of LCB were studied (series 4). Because both ethylene and ENB influence the retention, the EPDM samples with a very similar chemical composition were selected to keep the influence of the chemical composition on the elution behavior constant. The amount of long chain branching was determined according to the procedure described by Booij et al. and is specified by the parameter Δδ [219]. Δδ decreases from about 50-60 for linear polymers to about 5 for very highly branched polymers. Figure 4.27 shows the elution behavior of EPDM samples vary in their degree of long chain branching.

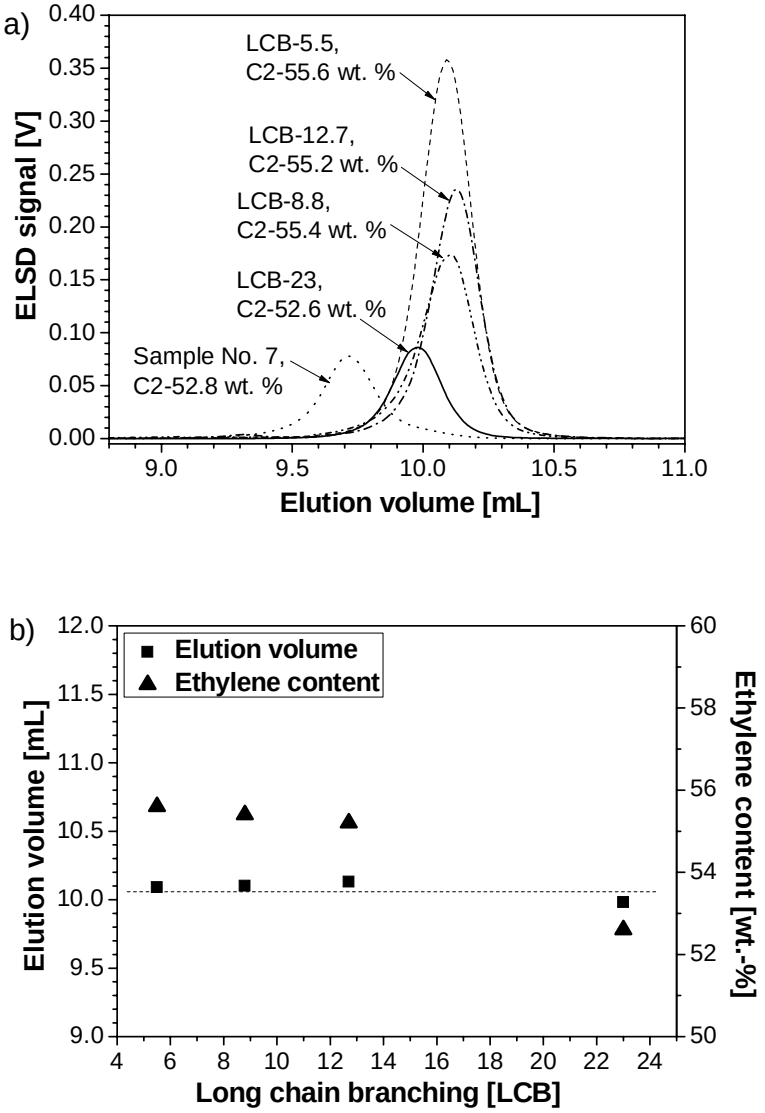


Figure 4.27: a) Overlay of chromatograms of EPDM samples which vary in their content of LCB, Δδ (Table 4.10) and b) long chain branching level versus elution volume and ethylene content of EPDM samples. Experimental conditions as in Figure 4.23.

The samples with similar ethylene content (i.e., ~55 wt. %) elute almost at identical elution volume thus proving that long chain branching exerts no influence on the elution volume (Figure 4.27). It is supposed that the long chain branches interact with the carbon sorbent in the same way as the main chain. On the other hand, short branches (pendant methyl, ethyl, butyl, hexyl or octyl groups) interrupt the interaction

of the main chain with the sorbent due to steric hindrance. Consequently, the elution volume decreases for samples with short chain branches as illustrated in Figure 4.23b, due to the steric hindrance given by the short chain branching. The same trend was found for copolymers of ethylene with 1-butene, 1-pentene, 1-hexene and 1-octene [104]. We assume that the obtained results are valid over a broad range of the chemical composition, because the incorporation of long chain branching does not necessarily affect the average chemical composition. Increasing the content of long branches in a macromolecule leads to a higher molar mass. It has already been shown that the difference in molar mass of those samples has no effect on the retention time (Figures 4.23 and 4.25). The smallest elution volume of the sample with the lowest ethylene content (sample No. 22, 52.6 wt. %) in this set of samples also confirms that the elution volume is mainly influenced by the ethylene content. These samples contain three different comonomers (ethylene, ENB, VNB), which may potentially be adsorbed. As the concentration of VNB or ENB is almost the same in all the samples, their contribution to retention of the samples is not seen from these results. Comparison of the elution volume of the EP sample No. 7 (9.7 mL), which has 52.8 wt. % ethylene, with the elution volume of the EPDM sample No. 22 (10.0 mL, Figure 4.27), which has almost the same ethylene content (52.6 wt. %), supports our above assumption that unsaturation (ENB or VNB) promotes adsorption.

4.3.4 Separation using ZirChrom-CARB/2-ethyl-1-hexanol→TCB

The chromatographic system ZirChrom-CARB/ 2-ethyl-1-hexanol → TCB has been shown to give pronounced retention of PE and ethylene/1-hexene copolymers with low comonomer content [211]. It is therefore of interest to probe its selectivity for EP- and EPDM copolymers. Figure 4.28 shows the chromatograms of EP-copolymers.

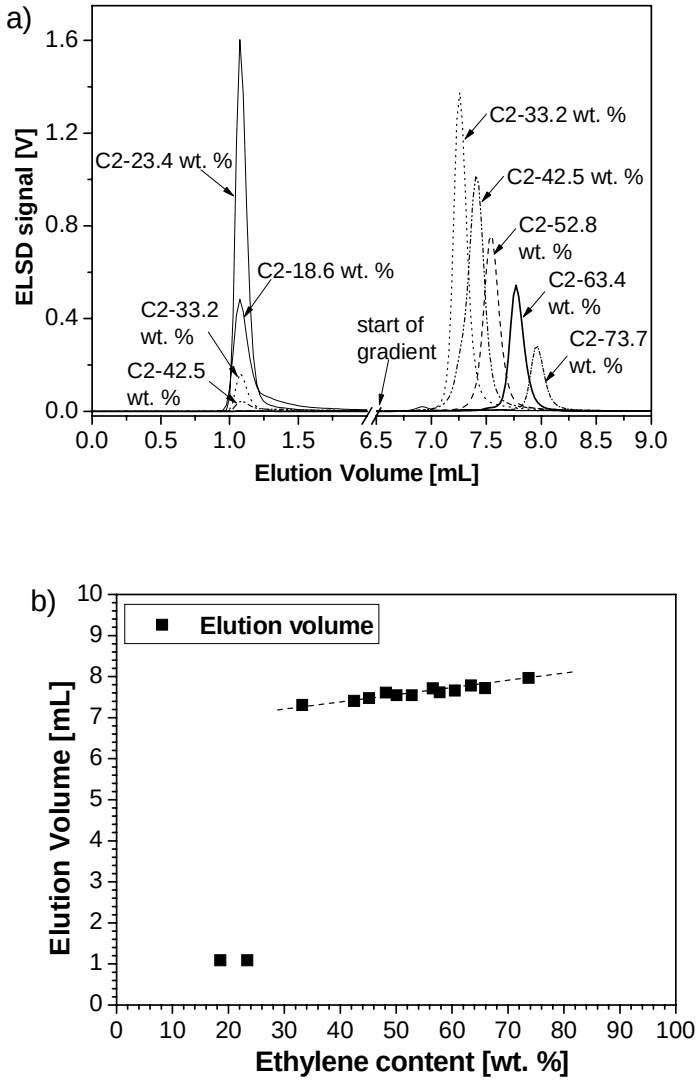
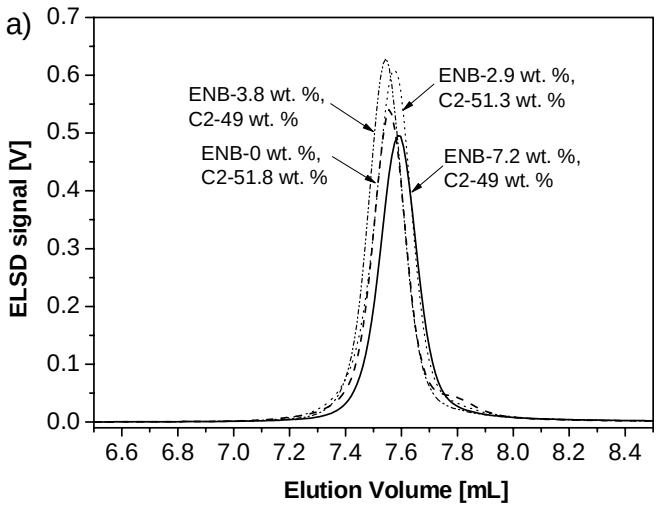


Figure 4.28: a) Overlay of chromatograms of EP rubbers and b) The average chemical composition (content of ethylene) versus elution volume of EP samples. Sorbent: ZirChrom-CARB; Mobile phase: gradient 2-ethyl-1-hexanol→TCB at a flow rate of 1 mL/minute; Temperature: 160 °C.

Unlike in the system Hypercarb/1-decanol→TCB the samples with a low ethylene content are not retained in ZirChrom-CARB/2-ethyl-1-hexanol→TCB. The sample with 18.6 wt. % ethylene elutes before the gradient, indicating that it is not adsorbed, and the samples with 33.2 wt. % and 42.5 wt. % ethylene elute in two peaks, one before and the other during the gradient. It can be speculated that the polymer chains

with lower ethylene content elute before the gradient and the chains with higher ethylene content elute latter in the gradient. However, the elution volume of the EP copolymers increases monotonously with the increase of the ethylene content in the other samples (Figure 4.28b). The elution volumes in this system are relatively lower than in Hypercarb/1-decanol→TCB, which shows that the strength of adsorption is lower compared to Hypercarb/1-decanol, hence the overall elution volume range in the gradient is lower. The sample with the highest ethylene content (73.7 wt. %) elutes at a retention volume of 8 mL, after TCB in the gradient reaches around 15 vol. %. The peak heights (or the peak areas) of the samples, which eluted in the gradient, decrease with increasing ethylene content (Figure 4.28) in the same manner as already observed previously (Figure 4.23a). This is due to the fact that the response of the ELSD may be function of the composition of the mobile phase and/or the chemical composition of the copolymers [48].

There is no significant difference in the elution volumes of EP copolymers which vary in their molar mass (series 2), confirming the results already found for the system Hypercarb/1-decanol→TCB. Figure 4.29a shows an overlay of the chromatograms of the third set of samples, which vary in their ENB content.



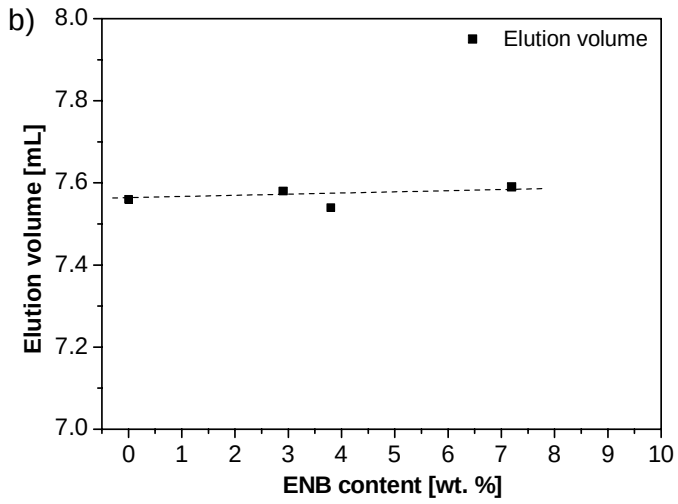


Figure 4.29: a) Overlay of chromatograms of EPDM samples which vary in their ENB content and b) ENB content plotted against elution volume and ethylene content. Experimental conditions as in Figure 4.28.

Different from the system Hypercarb/1-decanol→TCB there is a very small increment in the elution volume with increasing ENB content in the tested range of the chemical composition (Figure 4.29b). From this we can conclude that the chromatographic system ZirChrom-CARB/2-ethyl-1-hexanol→TCB is less selective to ENB.

Finally the influence of the degree of long chain branching on the elution volume was studied. The results are shown in Figure 4.30.

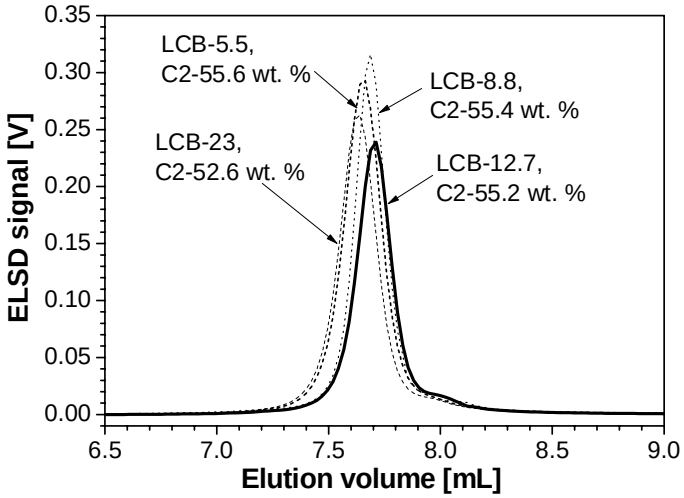


Figure 4.30: Overlay of chromatograms of EPDM samples which vary in molar mass and long chain branching. Long chain branching (LCB) is expressed in parameter Δδ (Table 4.10). Experimental conditions as in Figure 4.28.

As observed with the previous system the degree of long chain branching does not influence the elution volume.

4.4 Separating ethylene-propylene-diene terpolymers according to the content of diene by HT-HPLC and HT 2D-LC

4.4.1 Aim of the study

The separation of EPDM according to the three monomer units is an important task, to understand and improve the macroscopic properties of these technically important elastomers. In particular a separation with regard to the content of diene is of extreme value because the distribution of the diene along and across the polymer chain determines the cross-linking behavior of EPDM.

Previous study showed that EP copolymers can be separated according to their content of ethylene and suggested for EPDM that in addition to the separation according to the content of ethylene a separation according to the content of ENB might also be possible. With the aim to quantify the contribution of ENB alone on the chromatographic retention, a large number of carefully prepared and well characterized model EPDM terpolymers covering a wide range of ENB content were selected. Apart from the influence of the content of diene on the chromatographic separation, influence of the nature of diene was also studied in this work.

In addition to that the developed chromatographic separation with regard to the chemical composition by HPLC was hyphenated with a separation with regard to molar mass by SEC and thus to realize the first comprehensive characterization of the molecular heterogeneity of EPDM.

4.4.2 Polymer samples

The EPDM samples for this study were prepared and characterized by Lanxess Elastomers, Geleen, The Netherlands. The average values of their chemical composition measured using FTIR and the molar mass (using SEC) are summarized in Table 4.11.

Table 4.11: Average chemical composition obtained from FT-IR analysis, M_w and D obtained by SEC of EPDM samples.

Ethylene-propylene-ENB terpolymers.

Sample No.	**ENB [mol %]**	**C2 [mol %]**	**C3 [mol %]**	**M_w [kg/mol]**	D
14	0.1	68.4	31.4	1200	2.0
15	0.3	69.1	30.5	1215	1.9
16	0.6	68.9	30.5	1235	2.0
17	1.1	68.1	30.8	1350	2.0
17H	1.1	68.1	30.8	951	2.5
18	1.7	68.6	29.8	1420	2.0
19	2.0	67.9	30.1	1355	1.9
20	2.5	68.1	29.4	1420	1.9
20H	2.5	68.1	29.4	980	6.2
21	3.4	67.4	29.1	1435	1.9
22	4.0	67.3	28.7	1390	2.0
23	6.0	66.6	27.5	1410	1.8
23H	6.0	66.6	27.5	870	6.2

Ethylene-propylene-ENB, VNB and DCPD terpolymers.

Sample No.	**ENB [mol %]**	**VNB [mol %]**	**DCPD [mol %]**	**C2 [mol %]**	**C3 [mol %]**	**M_w [kg/mol]**	D
24	0.3	-	0.3	54.4	45.0	472	1.9
25	-	-	1.0	62.4	36.6	580	1.8
26	-	-	1.8	64.1	34.1	632	2.0
27	-	0.9	-	63.6	35.5	1026	2.8
28	-	0.3	-	66.0	33.7	746	2.1

Symbols: C2 – units corresponding to ethylene; C3 - units corresponding to propylene; M_w – weight average molar mass; D –dispersity, M_w/M_n.

It is supposed that the EP and EPDM samples used have a similar intramolecular structure in terms of sequence distribution statistics (i.e. randomness) and tacticity, because the same catalyst was used for their preparation.

The following procedure was used to hydrogenate EPDM 17, 20 and 23, to yield 17H, 20H, 23H: 250 mg of the sample was dissolved in 10 ml toluene and hydrogenated using (80 – 400 mg) p-toluenesulfonyl hydrazide corresponding to 10 equivalents in relation to the ENB amount at 135 ºC during 30 hours under 0.5 bar nitrogen. After hydrogenation the mixture of dissolved polymer and catalyst was precipitated in ice cold acetone and dried under vacuum. Analysis by ^{1}H NMR exhibited the complete absence of the double bonds. Before analysis the polymer sample was filtered to remove some undissolved gel like material.

4.4.3 HPLC of EPDM with different content of diene

It was previously [217] shown (Chapter 4.3) that the content of ethylene governs the elution behavior of EP copolymers and that the retention increases linearly with the ethylene content in this chromatographic system (Figure 4.31a), basically unaffected by their molar mass. The samples of EPDM which vary in their content of diene and ethylene were separated (Figure 4.31b) using the same experimental procedure as shown in Figure 4.23, Chapter 4.3.

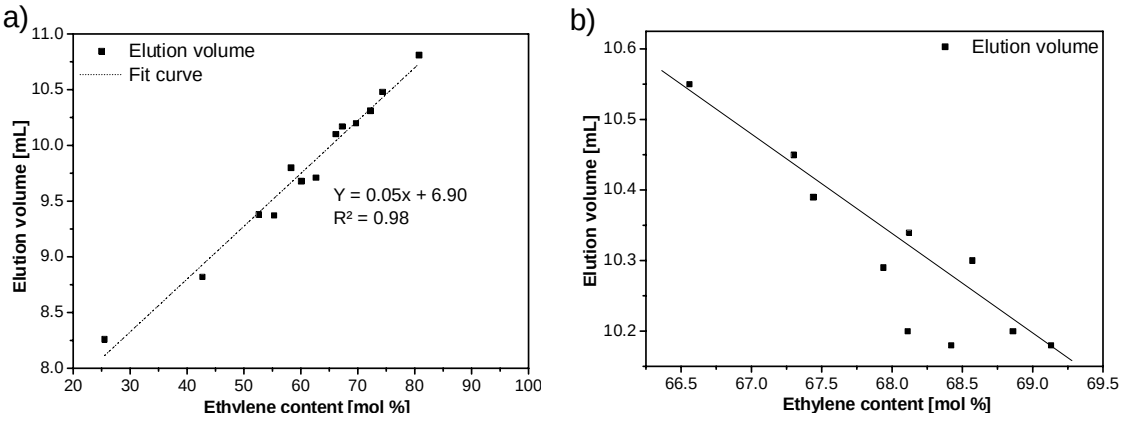


Figure 4.31: Elution volume at peak maximum as a function of the average ethylene content of a) EP samples and b) EPDM samples with ENB as termonomer (Table 4.11). Sorbent: Hypercarb; Mobile phase: gradient 1-decanol→TCB at a flow rate of 1 mL/minute; Temperature: 160 °C.

Unlike for the EP copolymers, the elution volume of the EPDM samples decreases even when the ethylene content increases (Figure 4.11b). It can therefore be assumed that this is due to the presence of diene, ENB. It is known that long chain branching may be present in the EPDM samples. Our previous experiments using EPDM samples with a known content of LCB have shown, however, that LCB does not influence the elution volume in this chromatographic system [217]. An overlay of chromatograms of EPDM samples which are identical with regard to their content of ethylene but differ in that of ENB is shown in Figure 4.32.

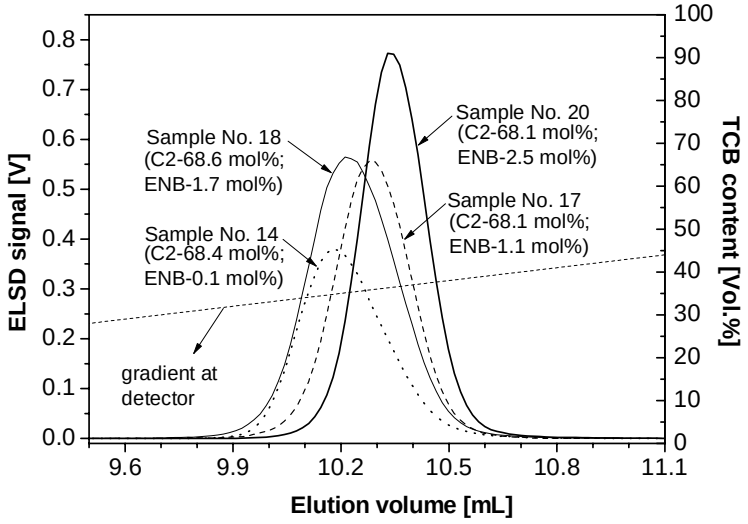


Figure 4.32: Overlay of chromatograms of EPDM samples. Notice: Gradient at the ELSD is indicated by dotted line.

Overlaying the chromatograms of the sample pairs 14/18 and 17/20 (which contain 68.4, 68.6 and 68.1, 68.1 mol % of ethylene and 0.1, 1.7 and 1.1, 2.5 mol % of ENB, respectively) reveals that the retention increases with the ENB content in both pairs. This indicates that ENB contributes to the retention of EPDM on Hypercarb and raises the question whether the nature of the diene also influences the retention. To probe this EPDM samples containing VNB and DCPD were separated using the same chromatographic system (Figure 4.33).

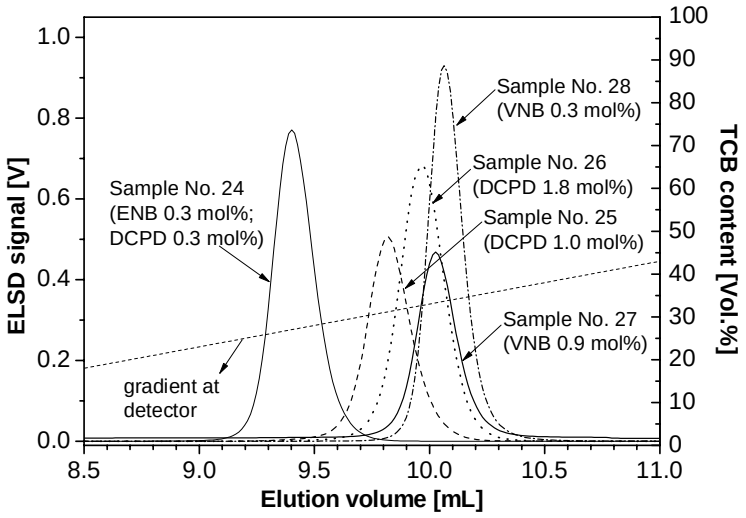


Figure 4.33: Overlay of chromatograms of EPDM samples which vary in their content of VNB and DCPD. Notice: The gradient at the ELSD is indicated by the dotted line.

Although the elution volume at the peak maximum changes, this can not be unambiguously allocated to the diene because the samples vary in their contents of both ethylene and diene. Therefore it is necessary to isolate the contribution of the diene to the retention to better understand its role on the elution behavior. To single out the contribution of ENB (VNB or DCPD) alone to the retention of the EPDM, the contribution of the methylene units to the adsorption has to be estimated first. The linear relationship between the retention volume and the ethylene content of EP copolymers (Figure 4.31a) can be used to calculate the elution volume of EP copolymers, if the average content of ethylene is known. Assuming that the contribution of the methylene units is independent from that of the diene units, the contribution of the methylene units solely (V_{EP}) was calculated using the dependence shown in Figure 4.31a. The difference between the experimentally found elution volume of an EPDM sample (V_{EPDM}) and the expected elution volume of an EP sample (V_{EP}) with identical ethylene content represents then the contribution of the diene units alone to the retention. This means that the absolute value of ethylene content in the EPDM copolymer is used and not a relative value on a C2/C3 basis. ΔEV (V_{EPDM} - V_{EP}) is plotted against the ENB (VNB or DCPD) content in Figure 4.34.

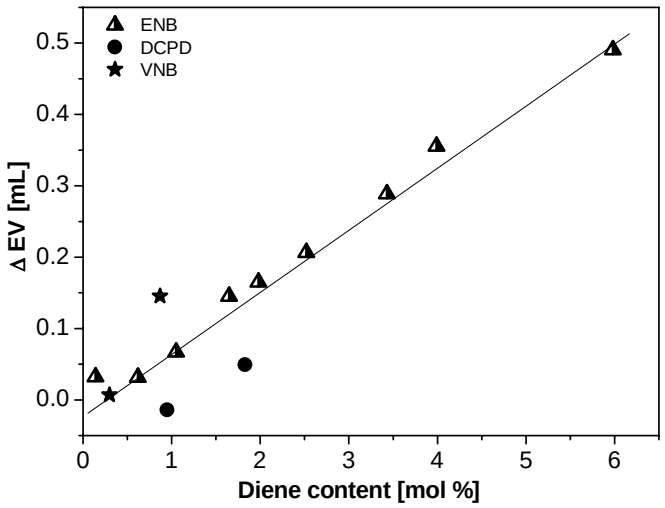


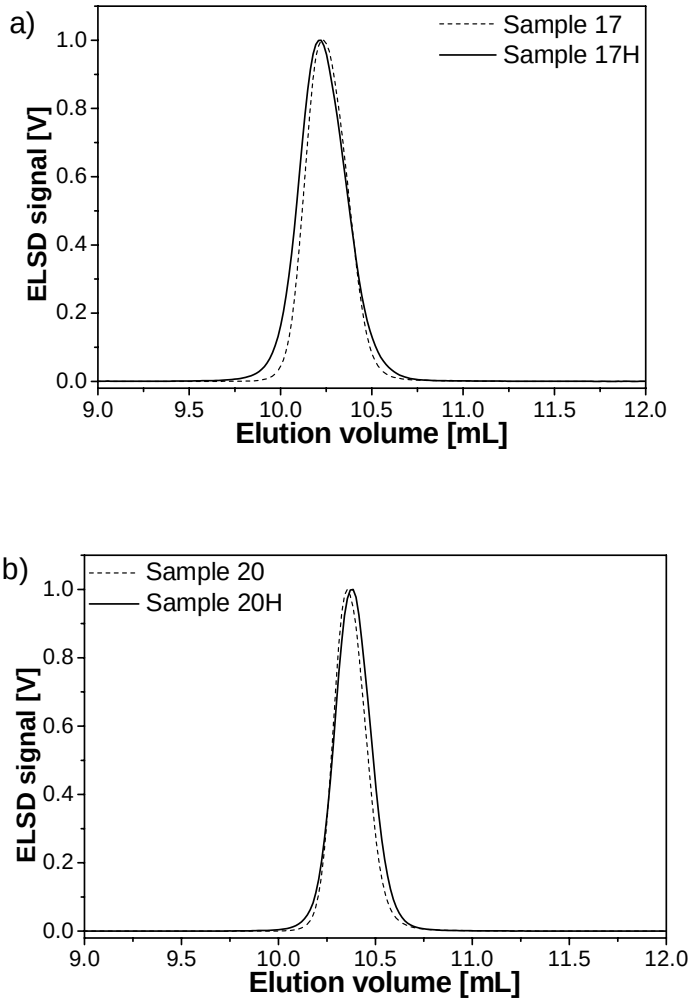
Figure 4.34: Difference (ΔEV) between elution volume of EPDM (V_{EPDM}) and expected elution volume of an EP sample (V_{EP}) with the same ethylene content as in EPDM.

ΔEV is a linear function of the content of ENB. Although the data available for VNB and DCPD does not allow to establish a systematic relationship it can be concluded that both dienes lead to an increased retention compared to the corresponding EP copolymer. Comparing ΔEV of EPDM samples with similar diene content indicates that the effect of DCPD is smaller than that of ENB, while the incorporation of VNB leads to stronger retention. The fact that sample 27 with 0.9 mol % VNB has a smaller elution volume than sample 28 with 0.3 mol % VNB (Figure 4.33) is caused by the different content of ethylene.

4.4.4 HPLC of hydrogenated EPDM

An important question is now to identify the driving force leading to the contribution of the dienes to the chromatographic retention. This might be due to an electronic interaction between the π-electrons of the dienic double bond and the aromatic system of the graphite. Alternatively the steric nature of the diene may favor the van der Waals interaction of the methylene chain with the graphite. With the aim to identify a possible electronic contribution of the double bond in the pendant diene unit on the retention, EPDM 17, 20, and 23 were completely hydrogenated. Overlays of

the chromatograms of EPDM 17H, 20H and 23H with that of the unhydrogenated starting samples are shown in Figure 4.35.



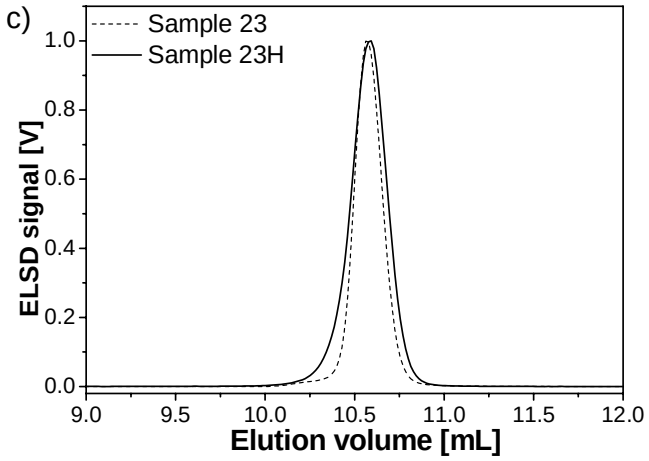


Figure 4.35: Overlay of the normalized elugrams of non-hydrogenated and hydrogenated EPDM of a) sample 17 and 17H, b) sample 20 and 20H, and c) sample 23 and 23H.

It is interesting to note that, even though there is a small variation in the peak broadness, i.e. the elugrams of hydrogenated ones are slightly broader, no difference in the elution volume at peak maximum can be observed between the hydrogenated sample and its non-hydrogenated counterpart. The slightly broader elugrams of the hydrogenated samples could be attributed to the loss of some sample in the form of gel during filtration after hydrogenation (see hydrogenation procedure above). These results suggest that the contribution of the diene to the retention (ΔEV) is primarily due to its structure and not the electronic contribution of the double bond. An alternative possible explanation may be changes in the microstructure (sequence distribution) of the EP backbone due to the incorporation of the diene. This in turn could alter the elution behaviour of the polymer chain.

4.4.5 Influence of molar mass on retention behavior

Figure 4.36 shows the influence of the molar mass on the elution volume of EPDM samples.

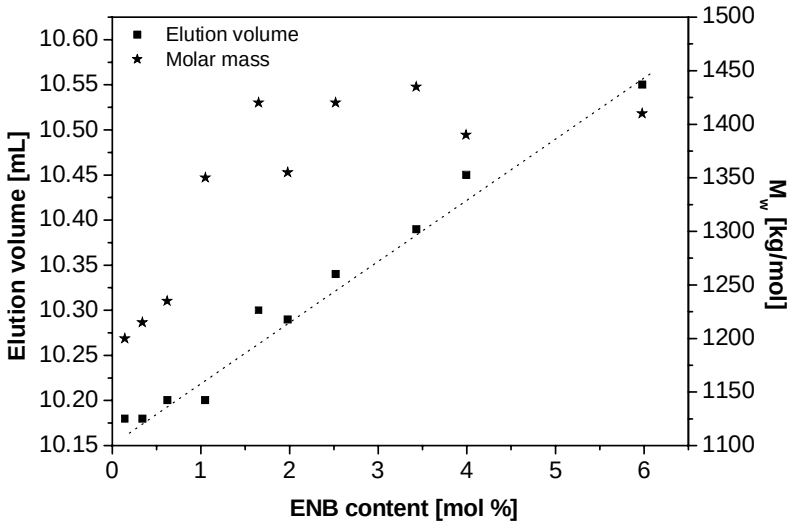


Figure 4.36: ENB content versus elution volume and weight-average molar mass (M_w).

While the elution volume of the samples increases linearly with the ENB content, the values of the weight-average molar mass prove that the system Hypercarb/1-decanol→TCB separates EPDM primarily according to the content of both ENB and ethylene and the retention of the samples is not influenced by the molar mass in the tested range (1200-1450 kg/mol). The absence of an effect of molar mass on the retention of EP copolymers was already established previously [217].

4.4.6 Influence of temperature on the retention behavior

Temperature can be used as an experimental parameter to control the retention of polymers [221-223]. The elution behavior of two EPDM samples (17 and 20) was probed at different temperatures to identify the influence of temperature on the chromatographic retention. These samples were chosen due to their similar ethylene content (68.1 mol %), which simplifies the understanding of the elution behavior. Figure 4.37 shows the elution volume at peak maximum as a function of temperature and the chromatographic resolution (R_S) at each temperature.

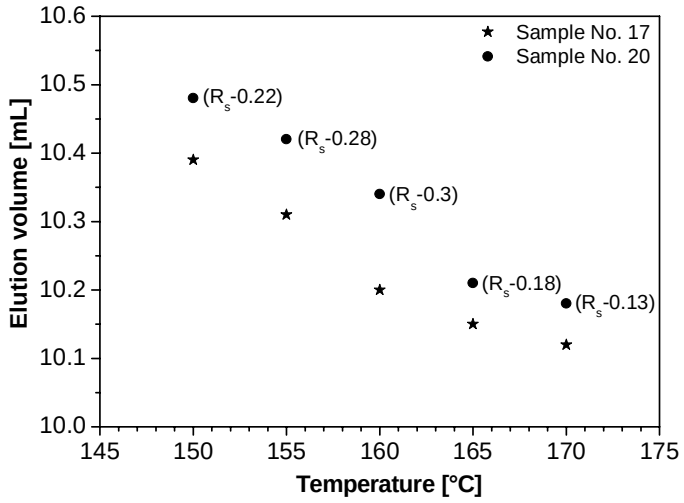


Figure 4.37: Influence of temperature on the elution volume of sample 17 and 20 and the chromatographic resolution (R_S) at that temperature.

The chromatographic resolution, which represents the quality of separation of two peaks, was calculated according to the equation:

$$R_S = \frac{2(t_2 - t_1)}{W_1 + W_2}$$

where t_1 and t_2 are elution times of the first and second and W_1 and W_2 are their baseline bandwidths [224].

The elution volume at the peak maximum decreases with increasing temperature for both samples in the tested temperature range 150-170 °C. This can be expected as the temperature counteracts the forces of adsorption [225]. R_S passes a maximum at 160 °C and drops when the temperature exceeds 160 °C.

4.4.7 Influence of solvent gradient on retention behavior

While the temperature influences the retention volume it has only a small affect on the chromatographic resolution. An alternative to improve the resolution of the separation would be to prolong the gradient as illustrated in Figure 4.38.

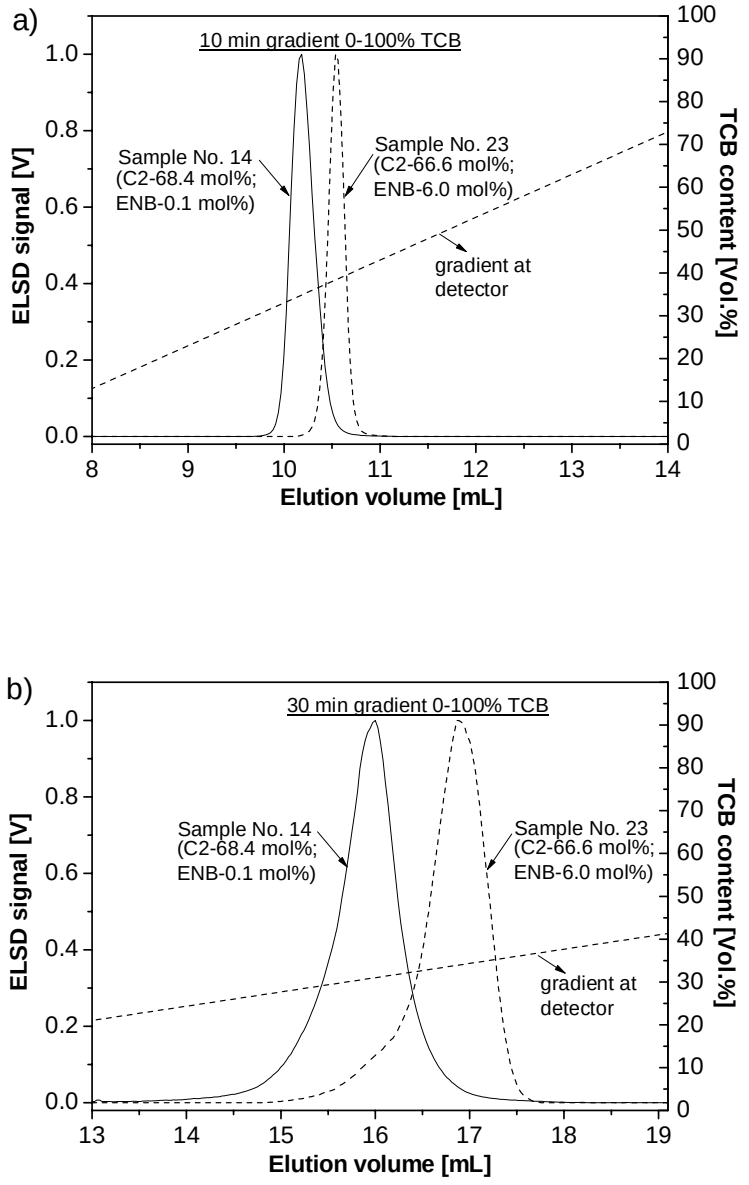


Figure 4.38: Overlay of chromatograms of samples 14 and 23 (C2 content 68.4 and 66.6 mol % and ENB content 0.1 and 6.0 mol %, respectively) obtained with different solvent gradient programs: a) Linear gradient from 0 to 100% TCB in 10 minutes b) Linear gradient from 0 to 100 % TCB in 30 minutes.

As a consequence of a flatter gradient the resolution between the peak maxima increases. Additionally differences in the shape of the peaks become recognizable. For example, while the chromatogram of sample 14 (ENB 0.1 mol %) represents an almost symmetric peak, that one of sample 23 (ENB 6.0 mol %) shows fronting. This

might be interpreted as a hint on differences in the CCD of the two samples. However, a quantitative interpretation of the detector signal requires its calibration because the ELSD response may be a function of the composition of the mobile phase as well as of the type of the analyte [226,227].

4.4.8 High-temperature two-dimensional liquid chromatography

The relationship between the chemical composition and the molar mass, also known as molecular heterogeneity, can be obtained by coupling the developed HPLC-method to SEC (HPLC × SEC). This allows to unravel the molecular heterogeneity of a polymer. Such separations were published for various polymers which are soluble at room temperature [228]. However, 2D-LC separations which require a high-temperature, i.e., 2D-LC of functionalized semicrystalline polyolefins [128], ethylene/1-octene copolymers [129] and polyolefin blends [130] were realized only recently. In the first step (HPLC) the macromolecules are separated according to their chemical composition, while in the second step (SEC) the obtained fractions are distinguished with respect to molar mass. Following a procedure described previously [128], the first dimension was calibrated with respect to ethylene content using selected EP copolymers, while the second dimension was calibrated with respect to the molar mass using linear PE standards. Figure 4.39 shows a linear correlation between the ethylene content and the elution volume of the EP copolymers at peak maximum.

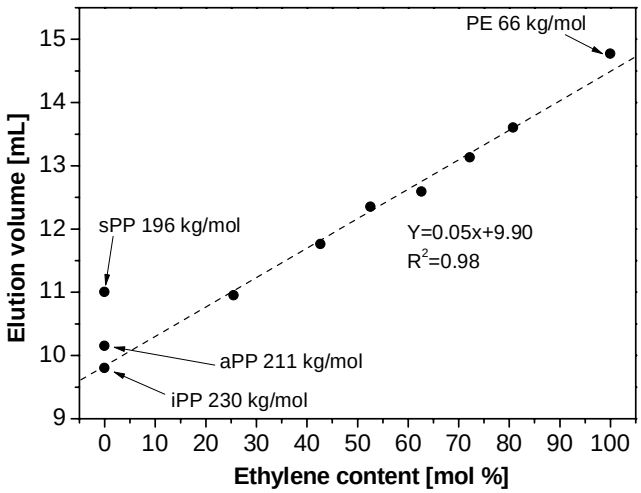


Figure 4.39: Average chemical composition (content of ethylene) versus elution volume of EP samples. Columns and flow rates: HPLC: Hypercarb®, 0.1 mL/min, Mobile phase: gradient 1-decanol→TCB; SEC: PL Rapide H, 2.5 mL/min. Temperature: 160 °C.

Although a similar calibration curve and an increase of retention with incorporation of ethylene were documented previously [217], this can be further refined: Extrapolating the fitted curve to 0 and 100 mol % of ethylene yields two boundary points. Extrapolation of the line towards an ethylene content of 100 mol % coincides with that of unbranched PE having an M_w > 20 kg/mol and the elution volume at the other end (corresponding to 0 mol % of ethylene) indicates that the propylene units present in the EP samples are isotactic.

Figure 4.40 and 4.41 show the contour plots corresponding to the HT 2D-LC separations of a blend of three EP copolymers and a blend of EPDM with EP, iPP and linear PE, where the x-axis represents the separation with respect to molar mass while the y-axis shows the elution according to chemical composition.

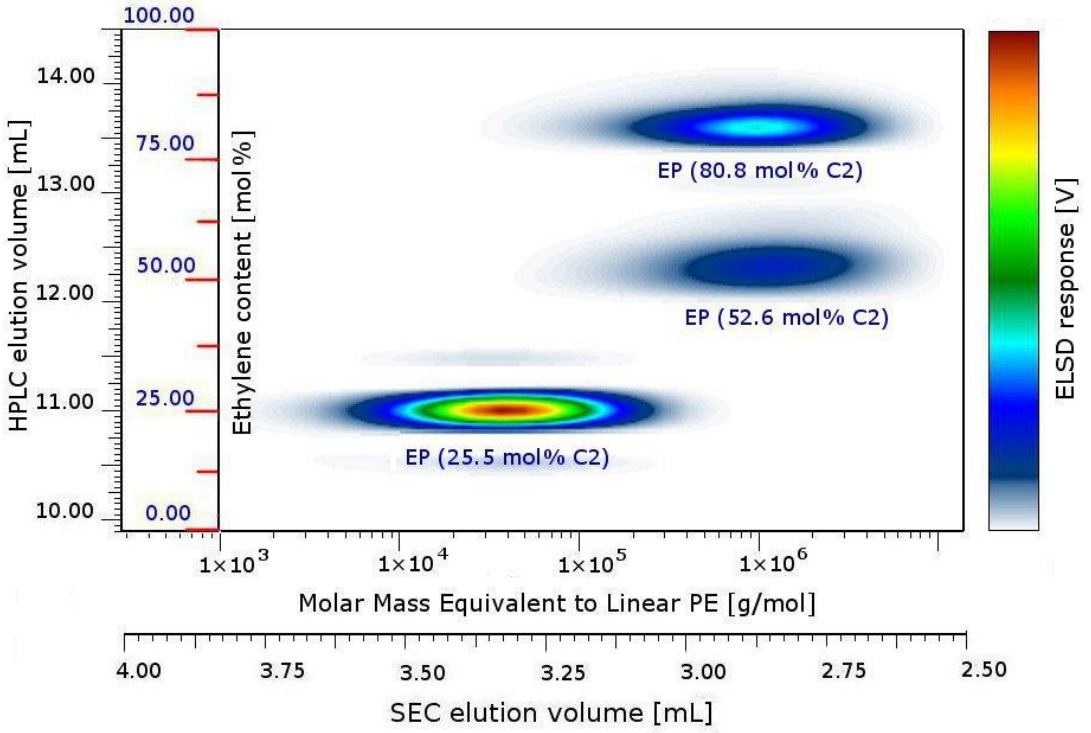


Figure 4.40: Contour plot obtained by HT 2D-LC of a blend of three EP copolymers (25.5 mol % of C2 (sample 1), 52.6 mol % of C2 (sample 3) and 80.8 mol % of C2 (sample 13). Experimental conditions as in Figure 4.39.

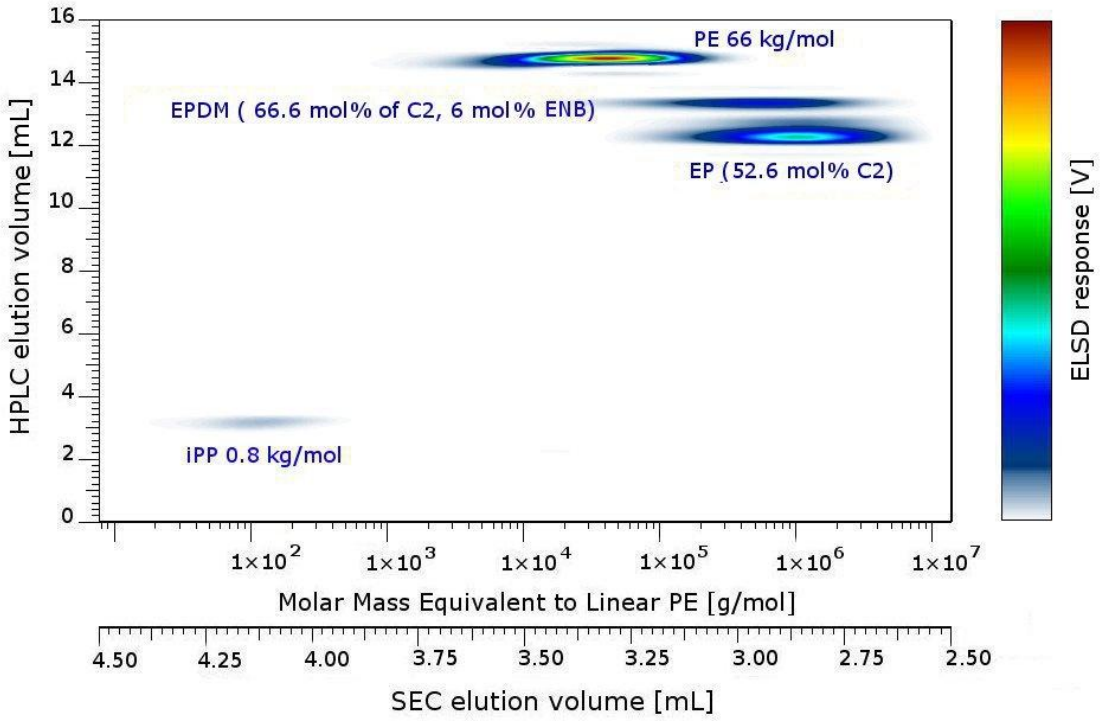


Figure 4.41: Contour plot obtained by HT 2D-LC of a blend of iPP 800 g/mol, EPDM (66.6 mol % of C2), PE 66 kg/mol, EP (52.6 mol % of C2). Experimental conditions as in Figure 4.41.

As can be noticed, all components of the blend are baseline separated. The HPLC separation of the EPDM in Hypercarb/1-decanol→TCB is a function of both ethylene and ENB content. On the other hand, EP copolymers are separated exclusively according to their content of ethylene, which is advantageous for interpretation of the contour plots. The hight of the peaks, i.e., the response of the ELSD, in the contour plots is colour coded. It was shown that the response of the ELSD is primarily a function of the concentration of the polymer solution and it may also depend on the composition of the mobile phase as well as on the type of the analyte [226,227]. Hence, for a precise quantitative evaluation of the concentration of the eluting components one should take these effects into account.

5 Experimental part

5.1 Cloud point

The cloud point measuring instrument was constructed at the Institute for Chemistry of Polymers (Montan University, Leoben, Austria). A glass tube with a polymer solution is thermostated in a heating block. A polymer sample of 8 mg was weighed into a glass tube and 8mL of a solvent was added. The polymer sample was dissolved at 160 °C or less than that for solvents with low boiling points. After dissolution of the polymer the temperature is gradually reduced. Transparency of the solution was continuously monitored. The intensity of the light which passes through the solution is measured by a photodiode. The polymer solution was vigorously mixed by magnetic stirring during the measurement. Sudden drift in the transparency of the polymer solution is taken as the cloud point temperature of polymer in that solvent. The assembly of the cloud point measuring instrument is shown in Figure 5.1.

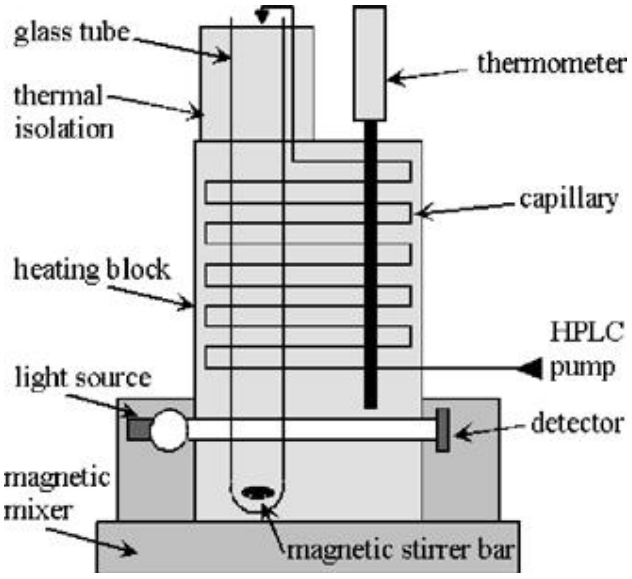


Figure 5.1: Schematic representation of apparatus used for the cloud point measurements [209].

5.2 High-Temperature SEC

A high temperature chromatograph PL 220 (Polymer Laboratories, Varian Inc, Church Stretton, England) was used to determine the molar mass distribution. The temperature of the injection sample block and of the column compartment was set at 140 °C. The flow rate of the mobile phase was 1 mL/min. The copolymers were dissolved for 2 h in 1,2,4-trichlorobenzene (TCB, cntaining 2 g/L butylated hydroxytoluene) at a concentration of 1-2 mg/mL at 150 °C. 200 µL of the polymer solution were injected. Polystyrene standards (Polymer Standards Service GmbH, Mainz, Germany) were used for calibration of a column set (3 columns Olexis, 250 x 8 mm, particle size 10 um, Polymer Laboratories, Varian Inc, Church Stretton, England).

5.3 High temperature chromatograph PL XT-220

A high-temperature chromatograph PL XT-220 high-temperature liquid chromatograph (Agilent Technologies, Santa Clara, CA) was used for all measurements unless otherwise mentioned. Injection of the sample was performed using a robotic sample handling system PL-XTR (Agilent Technologies). The temperature of the sample heating block, injection needle, injection port and the transfer line between the autosampler and the column compartment was adjusted to the respective solvents used: 160 °C for alcohols, TCB and 1,2-dichlorobenzene (ODCB); 140 °C for tetralin, mesitylene and decalin and 130 °C for xylene and p-xylene. An evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories) was used for detection. The ELSD was run at a nebulization temperature of 170 °C for n-hexylacetate, EGMBE and n-decane, 160 °C for cyclohexanone, cyclohexylacetate, tetralin, mesitylene, decalin, alcohols, TCB and ODCB and 130 °C for xylene and p-xylene. The evaporation temperature in the ELSD was set at 200 °C for cyclohexanone, n-hexylacetate, EGMBE and n-decane, 260 °C for cyclohexylacetate, alcohols, TCB and ODCB; 220 °C for tetralin, mesitylene and decalin, and 170 °C for xylene and p-xylene. An air flow rate of 1.5 L/min was used in ELSD. WinGPC-Software (Polymer Standards Service GmbH, Mainz, Germany) was used to collect and process the data. The flow rate of the

mobile phase was 1 mL/min. WinGPC-Software (Polymer Standards Service GmbH, Mainz, Germany) was used for data collection and processing. Figure 5.2 and 5.3 show the setup of high-HPLC system and a view of the column compartment.

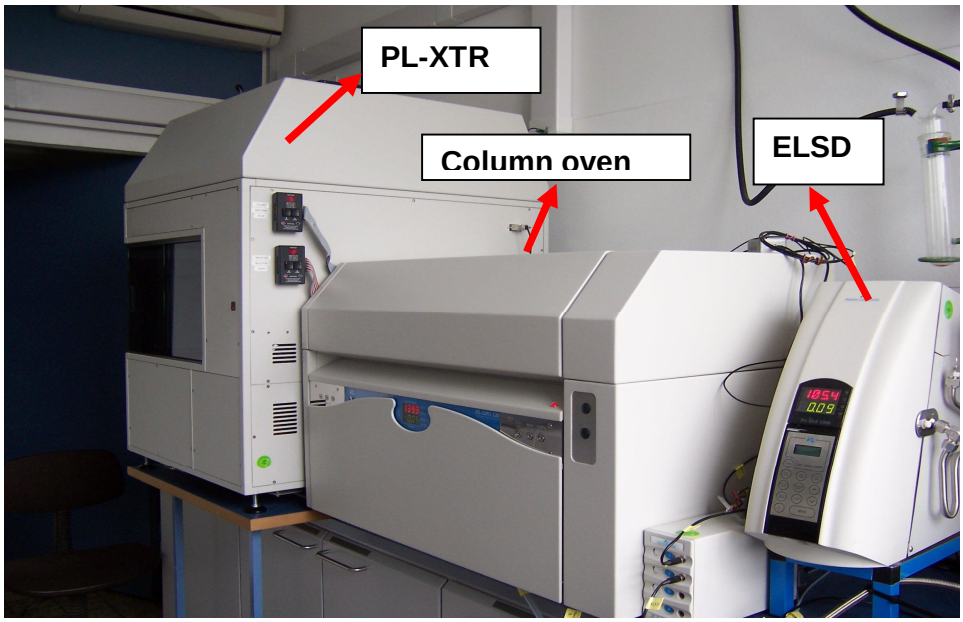


Figure 5.2: Set up of high-temperature HPLC system (PL XT-220).

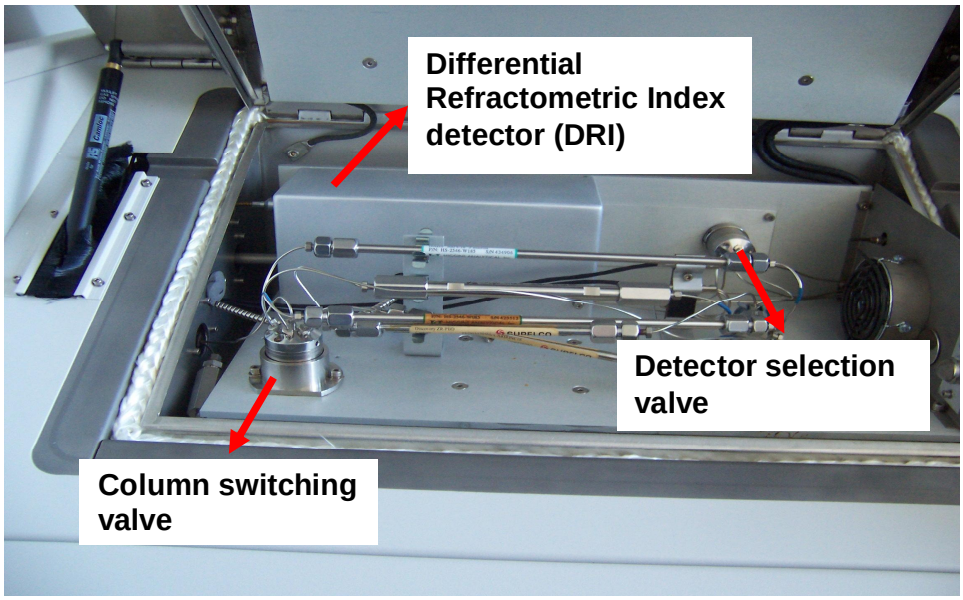


Figure 5.3: View of the column compartment with 6 columns attached to the column switching valve and detector selecting valve.

5.4 High temperature chromatograph PL-GPC 210

A part of the measurements was realized using the high-temperature liquid chromatograph PL-GPC 210 (Polymer Laboratories, Varian Inc, Church Stretton, United Kingdom). As detector a second ELSD (model PL-ELS 1000, Polymer Laboratories) was used. The gas leaving this ELSD was cooled in a metal tube (10 m x 1 cm I.D.), which was poured into circulating water at temperature 10 °C. This cooling ensured the condensation of 1-decanol. All other experimental parameters were the same as described for the chromatograph PL XT-220.

We noticed that the used ELSD detectors may have very different responses, which depends on the selected output signal (1/1 or 1/10 of the original signal), on the adjustment of a needle in the evaporator as well as on the purity of the glass lenses and the evaporator tubes.

5.5 High-temperature two-dimensional LC

All experiments were realised using a prototype chromatographic system for high-temperature two-dimensional liquid chromatography constructed by PolymerChar (Valencia, Spain), comprising an autosampler, two separate ovens, valves and two pumps equipped with vacuum degassers (Agilent, Waldbronn, Germany). One oven was used for thermostating the SEC column, while the second one, where the injector and a switching valve were housed, was used to thermostat the HPLC column. A scheme of the HT 2D-LC setup is shown in Figure 5.4.

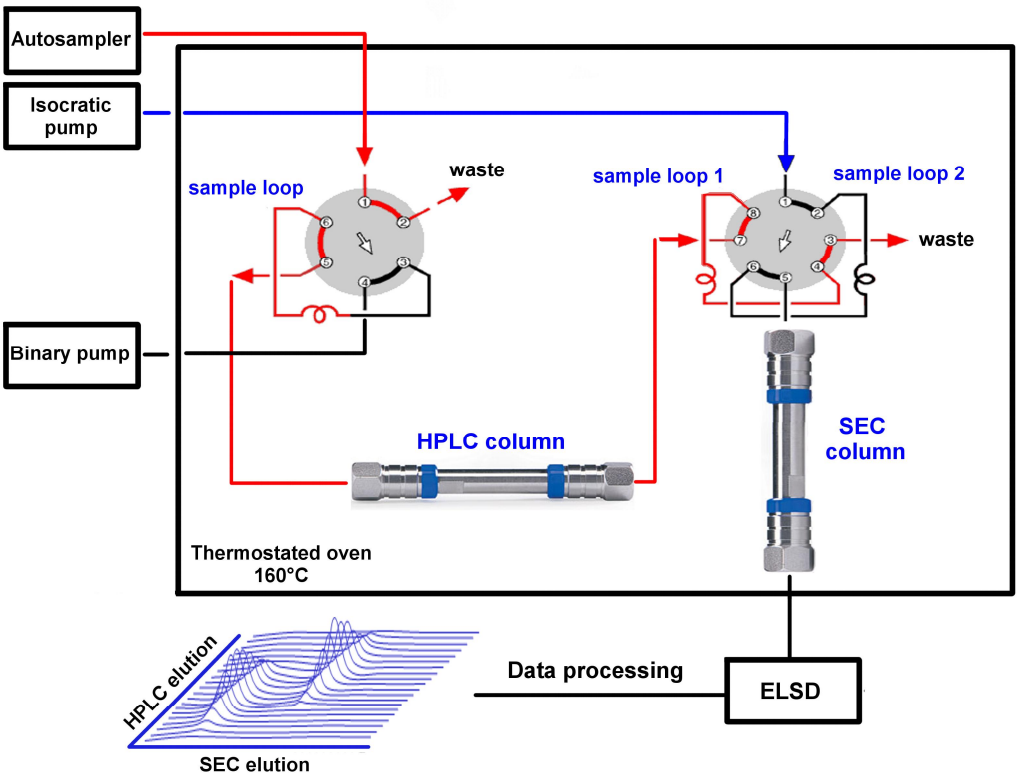


Figure 5.4: Scheme of the high-temperature two-dimensional LC setup.

The HT-HPLC and HT-SEC columns were coupled by an electronically controlled eight-port valve system EC8W (VICI Valco instruments, Houston, Texas, USA) equipped with two 200 µL loops. From the moment of injection into the HPLC column (100 µL injection loop), the 8-port valve was switched every 2 min in order to inject 200 µL of effluent from the HPLC into the SEC column.

The effluent from the SEC column was monitored by an evaporative light scattering detector (ELSD, described in the previous paragraph). Both ovens, the autosampler as well as the transfer line between the autosampler and the columns and the ELSD, were thermostated at 160 °C. The 2D-LC was handled by software provided by Polymer Char (Valencia, Spain). WinGPC 7.0 (Polymer Standards Service, Mainz, Germany) was used for data acquisition and evaluation.

5.6 Stationary phases for HT-HPLC of polyolefins

Four different carbon sorbents were used as the column packing:

A Hypercarb column (Thermo Scientific, Dreieich, Germany) containing particles of porous graphitic carbon with a particle diameter of 5 µm, surface area of 120 m^2/g, pore size of 250 Å and column dimensions 100 x 4.6 mm i.d. was used.

Carbon-clad zirconia particles (ZirChrom-CARB column) with a diameter of 5 µm and a column dimension of 100 x 4.6 mm I.D was purchased from ZirChrom Separations, Anoka, MN, USA.

Activated carbon TA 95 (PICA, Vierzon, France) with particle diameter about 1 mm, a surface area 1585 m^2/g and an average pore diameter of about 8 Å The carbon particles were dry-packed in a column with dimensions 150 x 4.6mm i.d.

Activated carbon TA 120 (PICA, Vierzon, France) with a particle diameter of 1 mm and surface area 1960 m^2/g was dry-packed into a column 150 x 4.6 mm I.D.

Exfoliated graphite was from SGL Carbon Co., Meittingen, Germany with irregular particles. It was dry-packed into a column 150 x 4.6 mm I.D by authors. Exfoliated graphite is produced from flaky graphite with a process in which graphite rapidly expands up to a couple of hundred times in volume, resulting in a puffed-up material with a very low density.

5.7 Stationary phases for high temperature two-dimensional LC

First dimension separations were carried out on a Hypercarb column packed with porous graphite particles with the following parameters: column size 250 × 4.6 mm i.d., average particle size diameter 5 µm, surface area of 120 m^2/g and pore size of 250 Å (Thermo Scientific, Dreieich, Germany). A column PL Rapide H, 150 × 7.5 mm (Polymer Laboratories, Church Stretton, England) was used in the second dimension (SEC).

5.8 Mobile phases

2-ethyl-1-hexanol, cyclohexylacetate, n-hexylacetate, cyclohexanone, EGMBE, n-decane, 1-decanol, Tetralin, decalin, p-xylene, xylene (mixture of 25 % o-Xylene, 46 % m-xylene, 21 % p-Xylene and 8 % ethyl benzene), ODCB, TCB, 1-heptanol, 1-octanol, 2-octanol and isononanol all of synthesis quality were obtained from Merck, Darmstadt, Germany. Mesitylene was supplied by ACROS, Geel, Belgium. The above solvents were used individually as the mobile phase. In selected cases a linear gradient from a pure respective solvent to TCB in 10 minutes was used to elute the polymer retained in the column. The gradient reaches the detector with a delay of 3.7 min with Hypercarb and 3.5 min with both ZirChrom-CARB and activated carbon TA 95 (after starting the gradient in pump) in the chromatograph PL XTR 220.

5.9 Polymer standards

Linear PE standards with M_w from 2 - 181 kg/mol were obtained from Polymer Standards Service (Mainz, Germany). PE with M_w = 260 kg/mol was purchased from PSD Polymers (Linz, Austria). iPP standards with an M_w ranging from 6 to 136 kg/mol were purchased from American Polymer Standards (Mentor, OH, USA). A sample of aPP with M_w = 315 kg/mol was donated by Dr. I. Mingozzi (LyondellBasell, Ferrara, Italy). sPP with M_w = 196 kg/mol was obtained from Sigma-Aldrich (Munich, Germany).

The weight average molar mass, dispersity ($D = M_w/M_n$) and average chemical composition of the polymer samples are summarized in Table 5.1.

Table 5.1: M_w, dispersity and average chemical composition of polymer samples.

PE standards

M_w (kg/mol)	**D**
1	1.2
2	1.1
16	1.4
36	1.8
60	1.5
260	2.9

PP standards

M_w (kg/mol)	**D**
iPP 1	1.1
iPP 60	2.4
iPP 136	3.7
sPP 196	2.4
aPP 315	2.6

The samples were dissolved in the respective mobile phase at a concentration of about 1-2 mg/mL. Time and temperature of dissolution were varied with solvent from 100 °C to 160 °C and 60 minutes to 180 minutes. 50 µL of each sample solution were injected.

6 Conclusions

Carbon-based sorbents were tested as stationary phase in combination with various solvents having high boiling points as mobile phase for liquid chromatographic separation of linear PE and PP. New sorbent/solvents systems, which enable the selective and reversible adsorption of PE and PP, were identified.

It was found that PE and/or PP adsorb to different extent, depending on the sorbent/solvent pair used. PE was most pronouncedly adsorbed on Hypercarb from 2-ethyl-1-hexanol, hexylacetate, cyclohexylacetate, n-decane, tetralin, and mesitylene; on ZirChrom- CARB from 2-ethyl-1-hexanol, 1-decanol, cyclohexylacetate, and hexylacetate; on TA 95 from hexylacetate, cyclohexanone and n-decane and on TA 120 from mesitylene. Complete adsorption of PE enabled to realize also the separation of blends of PE and PP and ethylene/1-hexene copolymers in ZirChrom-CARB and Hypercarb using a solvent gradient 2-ethyl-1-hexanol→TCB. The copolymers eluted according to their chemical composition in these chromatographic systems. However, ethylene/1-hexene copolymers with high content of 1-hexene (more than 26 mol %) elute without retention in ZirChrom-CARB.

In the case of PP the nature of the carbon sorbent strongly influences the extent of adsorption, with Hypercarb showing the strongest adsorption. While the system Hypercarb/alcohol→TCB enabled to separate PP with different tacticity, Hypercarb in combination with other solvents leads to partial adsorption or no adsorption of all PP stereoisomers. However, unlike in Hypercarb/1-decanol where the isotactic stereoform eluted in SEC mode, it adsorbed on Hypercarb from 1-heptanol, 2-octanol, 1-octanol or isononanol and eluted only in the gradient with TCB. ZirChrom-CARB and other carbons did not retain isotactic, syndiotactic or atactic PP from any of the tested solvents, i.e. they show a poor stereoresolution. Elution of PP in SEC mode enabled to realize superior separation of PP from PE, as it was demonstrated using ZirChrom-CARB and from 2-ethyl-1-hexanol→TCB gradient.

The chromatographic separation of ethylene/1-olefin copolymers with different side chain length demonstrates that short chain branches play an important role in adsorption of polyolefins and the adsorption varies with the SCB length. It was

observed that the SCB hinders the retention of the polymer molecule and the drop in elution volume (or retention) increases with increasing SCB content as well as the number of carbon units in the SCB. However, it turned around in the case of 1-octadecene as comonomer i.e., the drop in elution volume is relatively less compared to the copolymers with equivalent comonomer containing carbon units C8 or less. This indicates that the SCB itself also contributes to adsorption of polymer when the side chain is sufficiently long. Studying the adsorption behavior of PE and PP on Hypercarb at different temperatures indicated that PE may be adsorbed on graphitic carbon sorbents from TCB and ODCB in a temperature range of 100 – 120 °C. The adsorbed polymers may be desorbed and eluted by raising the temperature to 150 – 160 °C. Thus the described new sorbent/solvent systems have different selectivity from previously known HPLC systems for the separation of PE and PP.

For the first time ethylene-propylene copolymers and EPDM samples could be separated according to their chemical composition using high-temperature liquid chromatography, which is based on selective adsorption and desorption of polymers in a chromatographic column at 160 °C. Porous graphitic carbon and carbon-clad zirconia show different chromatographic selectivity: Porous graphitic carbon (Hypercarb) selectively interacts with the ethylene monomer units, when a gradient 1-decanol→TCB was used and the ethylene-propylene copolymers elute in the gradient according to their ethylene content. In the case of EPDM, the retention volume is a function of the content of both ethylene and ethylidene-2-norbornene. On the contrary, carbon-clad zirconia (ZirChrom-CARB) with a solvent gradient 2-ethyl-1-hexanol→TCB separated EP- and EPDM-copolymers mainly according to the ethylene content.

Moreover, interactive liquid chromatography using Hypercarb/1-decanol→TCB separates EPDM terpolymers according to their diene content. It was found that the contribution of the diene to the retention varies with the nature of diene. Calculating the difference between the experimental elution volume of EPDM and the expected elution volume of an EP copolymer with corresponding ethylene content enables to identify the contribution of the diene (ENB, VNB or DCPD) to the retention alone. Thus a separation of EPDM with regard to the content of diene becomes possible for the first time. Studying the retention of hydrogenated EPDM and comparing it to that

of the non-hydrogenated equivalent proves that the contribution of the diene to the chromatographic retention is primarily not due to the electronic contribution of the double bond. The reason may be either a structural selectivity of the graphite for the cycloaliphatic ring or an effect of the cycloaliphatic ring on the chain conformation of the macromolecule which facilitates the adsorption of the methylene units on the graphite. The molar mass and long chain branching of the polymer samples do not show any influence on the HPLC separation in the tested range.

Hyphenating the described HPLC separation with SEC enables for the first time to characterize the full molecular heterogeneity, i.e. the relationship between CCD and MMD, of EPDM for the first time. The differences between the samples are visualized in the contour plots.

The presented work enlarges substantially the number of HPLC sorbent/solvent systems suitable to realize high temperature adsorption liquid chromatography of polyolefins. Some sorbent/solvent pairs described in this work have a potential to be applied for a routine analytical and/or preparative LC separation of polyolefins. For example, the system Hypercarb/2-octanol→1,2,4-TCB enables to separate EP-copolymers according to their chemical composition in a range of 0 – 100 wt.% of ethylene. In contrast to TREF and CRYSTAF, HPLC requires smaller amount of samples, solvents and shorter time for analysis. Moreover, because HPLC separation is based on the selective adsorption and desorption of polyolefins, amorphous as well as semicrystalline polyolefin samples are selectively separated. HPLC analysis enables to verify, if the average chemical composition obtained from NMR spectroscopy corresponds to the copolymer alone or to a blends of both copolymer and homopolymer(s) or eventually to a mixture of both homopolymers. These results prove the potential of the adsorption HT-HPLC to be used as a valuable tool in establishing structure↔property relationships of polyolefins.

7 Abbreviations and symbols

2D-LC	Two dimensional liquid chromatography
aPP	Atactic polypropylene
a-TREF	Analytical temperature rising elution fractionation
CCD	Chemical composition distribution
CEF	Crystallization elution fractionation
CRYSTAF	Crystallizaiton analysis fractionation
CVD	Chemical vapour deposition
C/ZrO_2	Carbon-clad zirconia
D	Dispersity
DC	Dynamic crystallization
DCPD	Dicyclopentadiene
DP	Degree of polymerization
DSC	Differential scanning colorimetry
EBA	Ethylene butyl acrylate
EGMBE	Ethylene glycol monobutyl ether
ELSD	Evaporative light scattering detector
EMA	Ethylene methyl acrylate
ENB	5-ethylidene-2-norbornene
EP	Ethylene propylene
EPDM	Ethylene propylene diene monomer
EVA	Ethylene vinyl acetate
FTIR	Fourier transform infrared
GC	Gas chromatography
GCB	Graphitized carbon black
GPC	Gel permeation chromatography
HD	1,4-hexadiene
HDPE	High density polyethylene
HPLC	High performance liquid chromatography
HT-HPLC	High temperature high performance liquid chromatography
iPP	Isotactic polypropylene
IR	Infrared spectroscopy
LAC	Liquid adsorption chromatography

LC	Liquid chromatography
LCCC	Liquid chromatography at critical conditions
LCB	Long chain branch
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MMD	Molar mass distribution
NMR	Nuclear magnetic resonance
ODCB	1,2-dichlorobenzene
ODS	Octadecylsilane
PE	Polyethylene
PGC	Porous graphitized carbon
PP	Polypropylene
PS	Polystyrene
p-TREF	Preparative temperature rising elution fractionation
RI	Refractive index
SCB	Short chain branch
SEC	Size exclusion chromatography
sPP	Syndiotactic polypropylene
TCB	1,2,4-trichlorobenzene
TREF	Temperature rising elution fractionation
VNB	Vinyl norbornene
ZrO_2	Zirconia

Symbols

C2	Ethylene
C3	Propylene
ΔG	Gibbs free energy difference
ΔH	Change in interaction enthalpy
ΔH_u	Heat of fusion per repeating unit
ΔS	Change in conformational entropy
Δδ	Content of long chain branching
K_d	Distribution coefficient
K_{LAC}	Contribution of adsorption to distribution coefficient
K_{SEC}	Contribution of size exclusion to distribution coefficient

M_n	Number average molar mass
M_w	Weight average molar mass
p	Molar fraction of the crystallizing unit
R	Universal gas constant
R_S	Chromatographic resolution
t	Elution time
T	Absolute temperature
T_c	Crystallization temperature
T_m	Equilibrium melting point of the polymer/diluent mixture
T_m^0	Melting point of the homopolymer
T_{mp}	Peak melting temperature
V_1	Molar volume of the diluent
v_1	Volume fraction of the diluent
V_i	Interstitial volume of the column
vol. %	Volume percent
V_P	Pore volume of the stationary phase
V_R	Retention volume of the analyte
V_u	Molar volume of the polymer repeating unit
wt. %	Weight percent
W	Baseline bandwidths
χ_1	Flory Huggins thermodynamic interaction parameter

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Erklärung

Declaration

Ich erkläre hiermit an Eides Statt, dass ich meine Dissertation selbstständig und nur mit den angegebenen Hilfsmitteln angefertigt habe.

I declare that I have made my dissertation independently and only with the specified tools.

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Ich erkläre hiermit, noch keinen Promotionsversuch unternommen zu haben.

I hereby declare that this Doctor thesis has not been submitted previously for a comparable academic award.

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